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Denko K.K., 1-1, Oonodai 1-chome, Midori-ku, Chiba-shi, Chiba 267-0056 (JP).

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(74) Agent: **OHIE, Kunihisa**; Ohie Patent Office, Horiguchi No.2 Bldg. 7F 2-6, Nihonbashi-Ningyocho_2-chome, Chuo-ku, Tokyo 103-0013 (JP).

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(71) Applicants (*for all designated States except US*): **NIP-PON HOSO KYOKAI** [JP/JP]; 2-1, Jinnan 2-chome, Shibuya-ku, Tokyo 150-8001 (JP). **SHOWA DENKO K.K.** [JP/JP]; 13-9, Shiba Daimon 1-chome, Minato-ku, Tokyo 105-8518 (JP).

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(72) Inventors; and

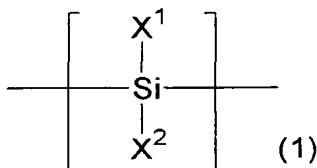
(75) Inventors/Applicants (*for US only*): **TOKITO, Shizuo** [JP/JP]; c/o NHK Science & Technical Research Laboratories, 10-11, Kinuta 1-chome, Setagaya-ku, Tokyo 157-8510 (JP). **SHIRANE, Koro** [JP/JP]; c/o SHOWA DENKO K.K., 1-1, Oonodai 1-chome, Midori-ku, Chiba-shi, Chiba 267-0056 (JP). **KAMACHI, Motoaki** [JP/JP]; c/o Showa

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(54) Title: PHOSPHORESCENT POLYMER COMPOUND, LIGHT EMITTING MATERIAL AND ORGANIC ELECTROLUMINESCENT (EL) DEVICE USING THE COMPOUND



(57) Abstract: The invention relates to a phosphorescent polymer compound enabling stable emission of blue phosphorescence with ultra-high quantum efficiency, comprising a phosphorescent repeating unit having phosphorescent property and a repeating unit represented by formula (1) below wherein X¹ and X² independently represent a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an amino group, a cyano group, a carboxyl group, a carbonyl group, a hydroxyl group, an aryl group, an aryloxy group or a heteroaryl group. The invention also relates to light emitting material and organic electroluminescent (EL) device using the compound.



WO 03/092334 A1

DESCRIPTION

PHOSPHORESCENT POLYMER COMPOUND, LIGHT EMITTING MATERIAL AND
ORGANIC ELECTROLUMINESCENT (EL) DEVICE USING THE COMPOUND

5

CROSS-REFERENCE TO THE RELATED APPLICATIONS

This is an application filed pursuant to 35 U.S.C. Section
111(a) with claiming the benefit of U.S. Provisional application
Serial No. 60/392,426 filed July 1, 2002, under the provision of
10 35 U.S.C. Section 111(b), pursuant to 35 U.S.C. Section 119(e) (1).

TECHNICAL FIELD

The present invention relates to a phosphorescent polymer
compound, light emitting material and organic electroluminescent
15 (EL) device using the compound.

BACKGROUND ART

An organic electroluminescent (EL) device is a device having
a sandwich structure where a thin organic film containing
20 fluorescent organic compound or phosphorescent organic compound
exists between a cathode and an anode. In such a device, excitation
of organic molecules is generated (formation of exciton) by
injecting holes and electrons into the thin organic film to
recombine the charges, and light (fluorescence/phosphorescence)
25 is emitted when the excited state moves back to the ground state.

The organic EL device is advantageous in that light luminance
of 10000 cd/m² or higher is achieved by applying a low voltage
of approximately 10V, and that selective use of organic polymer
enables emission of light from red to blue. Organic EL device,
30 being self-luminous and not angle-dependent, enables a wide field
of view and display with excellent visibility. Expectations are
placed on organic EL device as leading candidates for future

full-color displays.

The simplest organic EL device has a structure where a light-emitting layer is sandwiched between an anode and a cathode. For the purpose of improving emission efficiency, a typical type of the organic EL device contains a triple-layer structure where
5 an electron-transporting layer is inserted between one electrode and the light emitting layer and an hole-transporting layer is inserted between the other electrode and the light emitting layer.

Organic molecules are excited in two states, singlet state
10 and triplet state. In the case of electrical excitation, the generation ratio of singlet excitation to triplet excitation is 0.25:0.75. It is generally said that fluorescence is emitted from the singlet excited state and phosphorescence is emitted from the triplet excited state. Generally, deactivation from the triplet
15 excited state occurs in a non-radiation process without light-emission.

Since the singlet excited state is generated in a low ratio (0.25) as described above, the maximum quantum efficiency is as low as 5% in an organic EL device using a fluorescent organic compound.
20 On the other hand, in the case of phosphorescent emission, with the high generation ratio (0.75) of the triplet excited state as described above, there can be expected emission efficiency three times higher than fluorescent emission.

A recent report (Appl. Phys. Lett., Vol. 75, page 4 (1999))
25 says that a very specific organic compound emits phosphorescence at room temperature, and that organic EL device using the compound has realized highly efficient emission.

The organic compound contains metal complex having platinum or iridium in the center of the chemical structure thereof as
30 phosphorescent compound, and the phosphorescent compound is doped to several-percent concentration into a host layer of carbazole or triazole compound. Highly efficient emission as high as 20%

has been achieved by an ingenious configuration of the device, attracting attention as a measure for attaining ultrahigh efficiency of emission.

On the other hand, vigorous studies are being made on polymer organic EL device which is expected to be advantageous for larger display panel, higher definition and cost reduction. Polymer, being soluble in organic solvents and the like, can be applicable in coating methods using polymer in form of solution, such as spin coating method, printing method and ink jet method. Among them, ink jet method is attracting more attention as a promising measure for display production.

Application of phosphorescence emission to such a polymer-type organic EL device would contribute to attaining light emission with higher efficiency.

For instance, there is a recent report (Polymer Preprints, Vol.41, No.1 p.770 (2000)) about polymer-dispersed light-emitting device (EL device) using a light-emitting layer where 30 mass% of oxadiazole compound having electron transporting property is mixed with several mass% of iridium complex having phosphorescent property, with hole-transporting polyvinylcarbazole being used as host material.

In this instance, light emitting mechanism determining light emission efficiency is assumed to be based on energy transfer from the singlet and triplet excited states of polyvinylcarbazole to the phosphorescent compound, or direct excitation by electron-hole recombination on molecules of the phosphorescent compound. In either event, in order for the phosphorescent compound to emit light with high efficiency, it is important that energy level of the host material in singlet and triplet excited states is high as compared to that of the phosphorescent compound, and the band gap is large.

DISCLOSURE OF INVENTION

However, in fabrication of the polymer-type organic EL device, apart from red or green phosphorescent light-emission which requires only low energy, when high energy is required like in the case of blue light emission, selection of appropriate host materials is difficult to make. In addition, hole mobility of polyvinylcarbazole is as low as 10^{-6} cm/Vs and is not sufficient. Therefore, development of a host material having high hole/electron transporting property, which can exhibit high energy level in the singlet and triplet excited states, with a difference in energy level from the ground state being great, is needed.

In the case of polymer-dispersed type light-emitting device (EL device), in order to solve a problem that low molecular weight material dispersed in host material is segregated or phase-separated, a polymer-base light-emitting material having a long-lasting stability is desired.

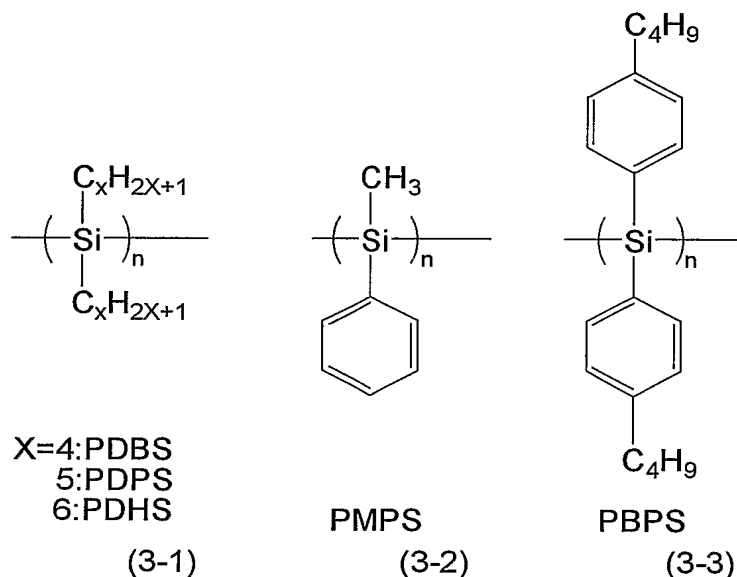
Accordingly, the present invention has been accomplished from the viewpoint of the above-mentioned problems, and one of the objects of the invention is to provide an organic polymer compound for use in organic EL device, having excellent stability, which enables phosphorescence emission with super high efficiency, especially in blue phosphorescent light emission.

Another object of the invention is to provide a light emitting material, organic electroluminescent (EL) device and display apparatus using the organic polymer compound.

In order to attain the objects of the invention, the present inventors has focused attention on a silicone-base polymer (polysilane), which has excellent hole transporting property and a large band gap.

Polysilane is a polymer comprising α -conjugated silicon one-dimensional chain as a main chain structure and substituents such as alkyl group and aryl group on side chains. Polysilane,

due to its electron system under quasi-one-dimensional conditions where the electrons are delocalized along the silicone one-dimensional chain, exhibits a high hole mobility on the order as high as 10^{-4}cm/Vs . This value is higher by two orders of magnitude than the mobility value of polyvinylcarbazole. Moreover, it is known that polysilane emits near-ultraviolet light based on its quasi-one-dimensional exciton. This means that polysilane has a large band gap. The electronic structure is changeable to a substituent structure as shown (3-1) to (3-3) below.



The band gap of poly(dibutylsilane) (hereinafter sometimes abbreviated as "PDBS") is 5.3eV while that of poly(bis(4-butylphenyl)silane) (hereinafter sometimes abbreviated as "PBPS") is 4 eV. Energy levels of the conducting band (corresponding to the lowest unoccupied molecular orbital) and valence band (corresponding to the highest occupied molecular orbital) varies depending on the band gap values. Polysilane, whose side chain can be readily substituted, allows a high degree of freedom in molecular design.

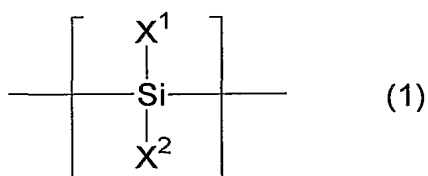
Therefore, it is assumed that, by using polysilane as host material in phosphorescent emission and allowing the polysilane to have an electronic geometry suitable for phosphorescent emission, efficient phosphorescent emission can be realized and display device which is stable even when continuously driven or overheated can be provided.

In addition, since polysilane is soluble in organic solvent and the solution can be used for forming a film on a substrate by a coating method, use of polysilane can be advantageous for fabricating large area display device.

Based on the above concept, the present inventors have invented a novel phosphorescent polymer compound by introducing a chemical structural unit having phosphorescent property into polymer chain of silicone-base polymer (polysilane).

That is, the present invention relates to:

1. A phosphorescent polymer compound comprising a phosphorescent unit having phosphorescent property and a repeating unit represented by formula (1):

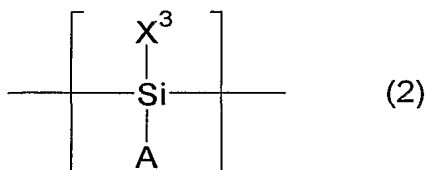


wherein X^1 and X^2 independently represent a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an amino group, a cyano group, a carboxyl group, a carbonyl group, a hydroxyl group, an aryl group which may be substituted, an aryloxy group which may be substituted or a heteroaryl group which may be substituted,

2. the phosphorescent polymer compound as described in item 1 above, wherein the number of the phosphorescent unit (m) and the number of the repeating unit represented by formula (1) (n) have the following relationship:

$$0.0001 \leq m/(m+n) \leq 0.5,$$

3. the phosphorescent polymer compound as described in item 1 or 2 above, wherein the phosphorescent unit is a unit having an organic phosphorescent group in the side chain and represented by formula (2) :



wherein X^3 represents a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an amino group, a cyano group, a carboxyl group, a carbonyl group, a hydroxyl group, an aryl group which may be substituted, an aryloxy group which may be substituted, or a heteroaryl group which may be substituted, and A represents an organic phosphorescent group,

4. the phosphorescent polymer compound as described in any one of items 1 to 3 above, wherein the phosphorescent unit has a complex structure of transition metal or rare-earth metal,

5. the phosphorescent polymer compound as described in any one of items 1 to 4 above, which is soluble in organic solvent or water,

6. the phosphorescent polymer compound as described in any one of items 1 to 5 above, having a polymerization degree of 5 to 5000,

7. a light-emitting material comprising the phosphorescent polymer compound as described in any one of items 1 to 6 above,

8. the light-emitting material as described in item 7 above, which further contains an organic compound having electron transporting property,

9. an organic electroluminescent (EL) device comprising one or more organic polymer layers between an anode and a cathode,

wherein at least one of the organic polymer layers comprises the light-emitting material as described in item 7 or 8 above,

10. the organic EL device as described in item 9 above, wherein the anode is formed on a plastic substrate,

5 11. the organic EL device as described in item 9 or 10 above, having the organic polymer layer(s) formed by a coating method, and

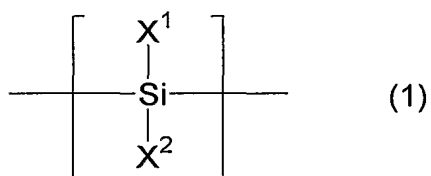
12. an active-matrix display apparatus comprising the organic EL device as described in any one of items 9 to 11 above and a
10 thin film transistor.

DETAILED DESCRIPTION OF INVENTION

Hereinafter, the present invention is described in detail.

I. Phosphorescent polymer compound

15 The present invention provides a phosphorescent polymer compound comprising a phosphorescent unit as a repeating unit emitting phosphorescent light and a repeating unit represented by formula (1) below:



20

wherein X^1 and X^2 each represent independently a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an amino group, cyano group, a carboxyl group, a carbonyl group, a hydroxyl group,
25 an aryl group, an aryloxy group, or a heteroaryl group.

In formula (1), the halogen atom represented by X^1 and X^2 is fluorine, chlorine, bromine or iodine.

The alkyl group represented by X^1 and X^2 preferably has 1 to 20 carbon atoms, more preferably 1 to 12 carbon atoms. Examples

of the alkyl group include methyl, ethyl, iso-propyl, tert-butyl, n-octyl, n-decyl, cyclopropyl, cyclopentyl and cyclohexyl.

The alkoxy group represented by X^1 and X^2 preferably has 1 to 20 carbon atoms, more preferably 1 to 12 carbon atoms. Examples
5 of the alkoxy group include methoxy, ethoxy, iso-propoxy and tert-butoxy.

The aryl group represented by X^1 and X^2 preferably has 6 to 30 carbon atoms, more preferably 6 to 20 carbon atoms. Examples of the aryl group include phenyl, naphthyl, anthracenyl and pyrenyl.

10 The aryloxy group represented by X^1 and X^2 preferably has 6 to 30 carbon atoms, more preferably 6 to 20 carbon atoms. Examples of the aryl group include phenyloxy, naphtyloxy, anthracenyloxy and pyrenyloxy.

The hetero aryl group represented by X^1 and X^2 preferably
15 contains at least one of oxygen atom, a nitrogen atom and a sulfur atom, and preferably has 1 to 50 carbon atoms, more preferably 1 to 30 carbon atoms. Examples of the hetero aryl group include imidazoryl, pyridyl, furyl, piperidyl, benzoxazoryl, thienyl, triazoryl and carbazoryl.

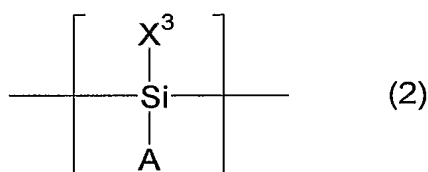
20 The phosphorescent polymer compound of the present invention has a copolymer structure as described above, and is hereinafter sometimes simply referred to as "copolymer".

The phosphorescent polymer compound of the present invention is stable and exhibits ultra-high efficiency in
25 phosphorescent-light emission.

Assuming that the repetition number for the phosphorescent repeating unit is m and that the repetition number for the repeating unit represented by formula (1) is n , the value of $m/(m+n)$ falls within the range of 0.0001 to 0.5, preferably 0.001 to 0.1. If
30 the value exceeds the range, in other words, the ratio of phosphorescent unit is higher, the light emission efficiency decreases due to a phenomenon called concentration quenching. The

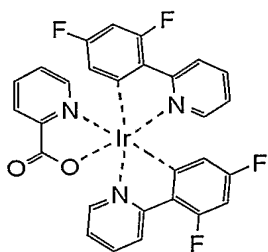
phosphorescent units are introduced in the polymer chains at random, however, in some cases, it is preferable that the units are introduced at uniform intervals or in blocks.

The phosphorescent unit to be introduced in the copolymer of the present invention may be introduced as the main chain or side chain. In the case where the phosphorescent unit is introduced in the side chain, it is preferable that the phosphorescent unit has a structure represented by formula (2) below.

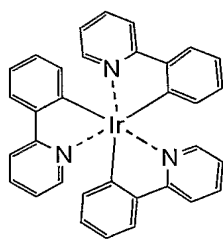


In formula (2), A represents a phosphorescent organic group, X^3 represents the same as X^1 and X^2 defined in formula (1), that is, a hydrogen atom, a halogen atom, an alkyl group, alkoxy group, an amino group, a cyano group, a carboxyl group, a carbonyl group, a hydroxyl group, an aryl group, an aryloxy group, or a hetero aryl group.

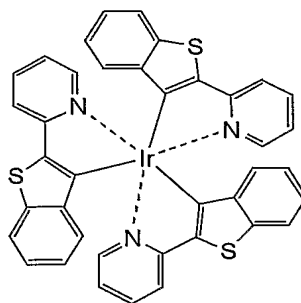
For the copolymer (phosphorescent polymer compound) of the present invention to exhibit high emission efficiency, it is preferable that the phosphorescent unit is a monovalent, divalent or trivalent group of transition metal or rare-earth metal complex. Examples of the phosphorescent unit include metal complexes having an organic ligand represented by formulae (4-1) to (4-5) below, however, are not limited thereto in the present invention.



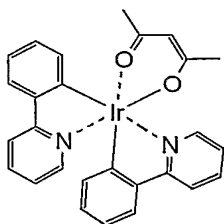
(4-1)



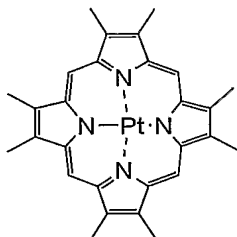
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(4-5)

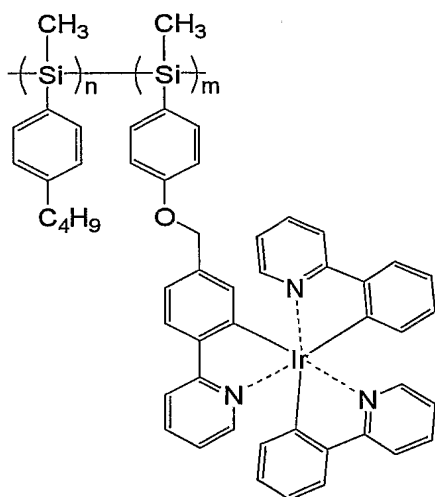
Examples of the ligand used in the transition metal or
 5 rare-earth metal complex include acetylacetonate,
 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine,
 1,10-phenanthroline, 2-phenylpyridine, porphyrin,
 phthalocyanine, pyrimidine, quinoline and derivatives thereof,
 however are not limited thereto. One or more kinds of such ligands
 10 are contained in one complex. Also, as the complex compound,
 binuclear complex, multinuclear complex, or composite consisting
 of two or more of these complexes may be used.

Examples of transition metal used for the transition metal
 complex above include metals from Sc (atomic number 21) to Zn (atomic
 15 number 30) in the first transition element series, Y (atomic number
 39) to Cd (atomic number 48) in the second transition element series,
 and Hf (atomic number 72) to Hg (atomic number 80) in the third
 transition element series.

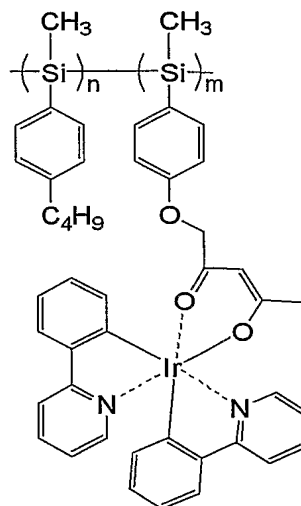
Examples of rare-earth metal used for the rare-earth metal
 20 complex above include metals from La (atomic number 57) to Lu (atomic

number 71).

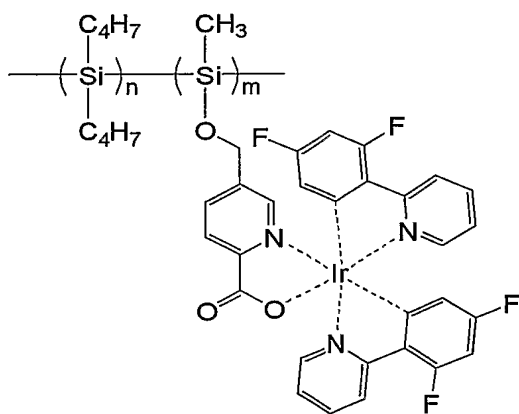
Specific examples of the structure of the copolymer (polymer) are illustrated by means of the following formulae (5-1) to (5-4) for those having the phosphorescent unit introduced in the side chain and formulae (6-1) and (6-2) having the phosphorescent unit introduced in the main chain, however, are not limited thereto.



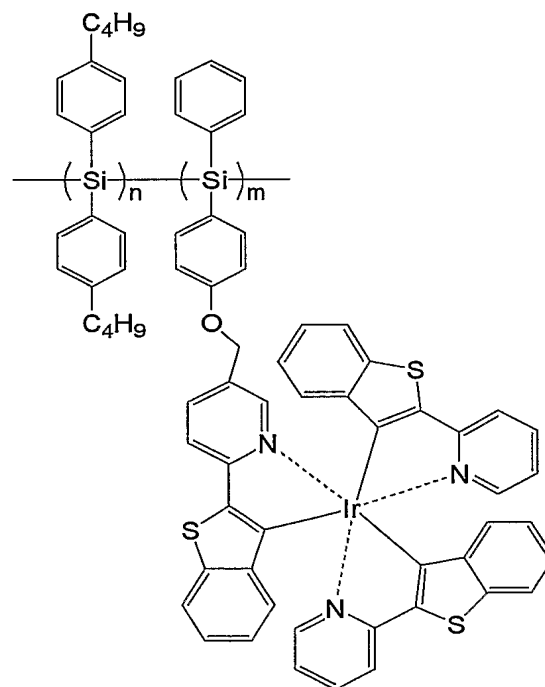
(5-1)



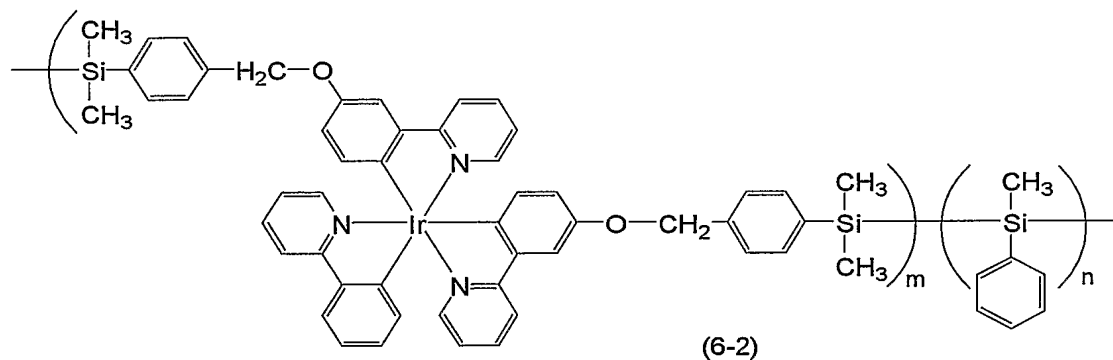
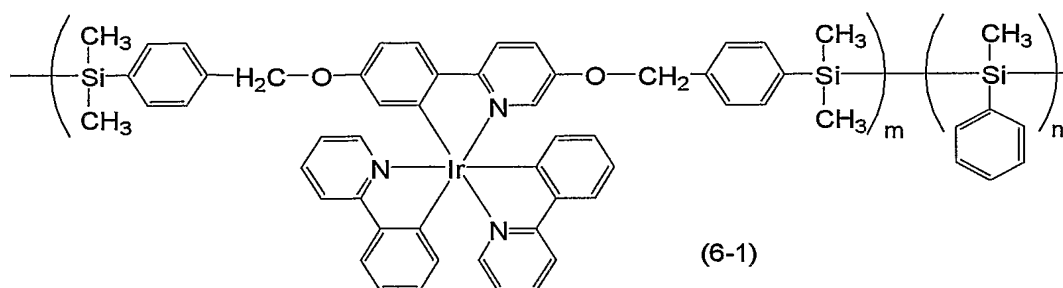
(5-2)



(5-3)



(5-4)



In the copolymer (polymer compound) of the present invention,
 5 the substituent in the polysilane unit is selected according to the electron geometry of the phosphorescent unit. For example, in the case of formula (5-4) where red light is emitted, PBPS, having a small band gap, is selected as a main structure. In the case of formula (5-3) where blue light is emitted, PDBS, having
 10 a large band gap, is selected as a main structure. Here, "main structure" indicates the portion "()n" in formula (1).

The polymerization degree of the copolymer (polymer compound) of the present invention is preferably within the range of from 5 to 5000. If the degree is lower than 5, a film formed
 15 using the copolymer can hardly be uniform and crystallization is readily caused, thereby deteriorating stability of the film. Polymer having a polymerization degree exceeding 5000 is difficult to be prepared, and such a polymer does not have good solubility in solvent. Accordingly, polymer having a polymerization degree

of 5 to 5000 is used for forming a uniform and stable film.

By using the copolymer (phosphorescent polymer compound) of the present invention, soluble in organic solvent, a thin uniform film can be formed on a substrate by coating method. Further, pattern forming in three primary colors is possible by printing method or ink jet method.

Next, production process of the copolymer (phosphorescent polymer compound) of the present invention is described in detail.

The polymer compound of the present invention can be synthesized by various known methods.

For example, in a case where a phosphorescent unit is introduced as a side chain of the polymer chain, the following phosphorescent unit precursor is synthesized first. That is, one or more functional groups such as an alkyl group, a hydroxyl group, a carbonyl group, an amino group, an isocyanate group and halogens are introduced to one of the ligands of a transition metal complex having phosphorescence-emitting property. These functional groups may be directly introduced to the transition metal complex. Also, a desired transition metal complex having functional groups in a ligand may be prepared by complex synthesis method such as ligand substitution or the method through binuclear complex after synthesizing a compound having these functional groups introduced to a ligand thereof. Secondly, to the transition metal complex having functional groups introduced therein, a compound such as dichlorosilane and trichlorosilane, which is to be a functional group introduced to a polysilane unit, is bonded, so that the ligand of the transition metal is connected to dichlorosilane by an appropriate bonding group having an appropriate length such as alkyl bond, ether bond, ester bond, amide bond and urethane bond. By this synthesis process, dichlorosilane derivative or trichlorosilane derivative to be a precursor of phosphorescent unit is synthesized.

The phosphorescent unit is further reacted with one or more appropriate dichlorosilanes such as dichlorodimethylsilane and dichloromethylphenylsilane, in an appropriate solvent such as benzene, toluene and xylene in the presence of an appropriate metal such as sodium, to thereby prepare the copolymer (polymer) of the invention. In this reaction, by changing reaction conditions such as concentration and ratio of the precursor of the phosphorescent unit and dichlorosilane, the kind of the solvent, the amount of the metal, reaction time, reaction temperature and the like, a variety of polymers which vary in the concentration ratio of the phosphorescent unit, molecular weight of the polymer and molecular weight distribution are obtainable. That is, the ratio of the phosphorescent unit to total polymer unit can be adjusted to the range of 0.0001 to 0.5, and also, the polymerization degree can be adjusted to the range of 5 to 5000.

Alternatively, in the case where a phosphorescent unit is incorporated in the main chain of the polymer chain, first the following precursor of a phosphorescent unit is synthesized. That is, functional groups selected from an alkyl group, a hydroxyl group, a carbonyl group, an amino group, an isocyanate group, halogen and the like are introduced to the plural ligands of a transition metal complex having phosphorescence-emitting property. The functional groups may be introduced directly to the transition metal complex. Also, a desired transition metal complex having functional groups introduced to ligands may be prepared by ligand substitution or by complex synthesis method through binuclear complex after synthesizing a compound having these functional groups introduced to ligands thereof. Secondly, to the transition metal complex having functional groups introduced therein, a compound, such as monochlorosilane, which is to be a functional group introduced to each ligand of a polymer unit, is bonded, so that the ligands of the transition metal is connected

to monochlorosilane, by an appropriate bonding group having an appropriate length such as alkyl bond, ether bond, ester bond, amide bond and urethane bond. By this synthesis process, a compound to be a precursor of the phosphorescent unit which has plural
5 monochlorosilane portions in one molecular is synthesized.

The precursor phosphorescent unit is further reacted with one or more appropriate dichlorosilanes such as dichlorodimethylsilane and dichloromethylphenylsilane, in an appropriate solvent such as benzene, toluene and xylene in the
10 presence of an appropriate metal such as sodium, to thereby prepare the copolymer (polymer) of the invention. In this reaction, like in the previously mentioned cases where in dichlorosilanes are used, by changing reaction conditions, a variety of polymers which vary in the concentration ratio of the phosphorescent unit, molecular
15 weight of the polymer and molecular weight distribution are obtainable. That is, the ratio of the phosphorescent unit to the total polymer unit can be adjusted to the range of 0.0001 to 0.5, and also, the polymerization degree can be adjusted to the range of 5 to 5000.

20 Another method for incorporating a phosphorescent unit into a polymer is that ligand portion of a transition metal complex is synthesized in advance, and then after reacting with an appropriate dichlorosilanes in the same manner as above, the transition metal is complexed on the ligand portion to thereby
25 obtain a desired polymer.

Moreover, as method for polymerizing polysilane, other than dechlorination condensation method, dehydrogenation condensation method (Coord. Chem. Rev., Vol.206-207, p.493 (2000)), anion
30 polymerization method (Macromolecules, Vol.27, No.8 p.2360 (1994)), electro-chemical polymerization method and the like are known (J. Macromol. Sci., Rev. Macromol. Chem. Phys., Vol. c38, No.4 p.637 (1998)). Applying to these methods, appropriate polymer

units can be prepared, and by the combination use of the units, desired polymer compound can be obtained.

Thus obtained polymer compound may be used as is, however, may be once or plural times subjected to purification process such as reprecipitation and column chromatography, which is to be selected according to properties of the polymer compound, to enhance the purity.

II. Light-emitting material

Next, light-emitting material comprising the copolymer (phosphorescent polymer compound) of the present invention is described below.

The copolymer (polymer compound) of the present invention itself can be used as light emitting material for organic EL device. Moreover, for the purpose of supplement the electron transporting property, the copolymer of the present invention may be mixed with other electron transporting compounds to be used as light emitting material.

Here, electron transporting compound to be mixed with the copolymer (polymer compound) of the present invention may be either low-molecular compound or high-molecular compound. Examples of low-molecular compound to be mixed with the polymer compound of the present invention include oxadiazole derivative, triazole derivative, imidazole derivative, triazine derivative and organic metal complex compound, but are not limited to those compounds. As high-molecular compound to be mixed with the polymer compound of the present invention, compounds polymerized by introducing polymerizable functional group into the above mentioned low-molecular electron-transporting compounds, for instance, polyPBD (PPBD) as disclosed in JP-A-10-1665, can be used, but are not limited to the compound.

Moreover, for the purpose of improving properties of a film

formed from the copolymer (polymer compound) of the present invention, other polymer compounds, which do not participate in light-emitting property, may be mixed with the polymer compound of the present invention to be used as light emitting material.

5 Examples of such a polymer compound include polymerthylmethacrylate (PMMA) which may be added for the purpose of imparting flexibility to the obtained film, but are not limited thereto.

10 III. Organic EL device

Next, the organic EL device using light emitting material comprising copolymer (phosphorescent polymer compound) of the present invention will be described.

The configuration of the organic EL device using the light
15 emitting material comprising the polymer compound of the present invention as a light-emitting layer may include, between an anode and a cathode, a structure selected from (1) hole transporting layer/light emitting layer/electron transporting layer, (2) hole transporting layer/light emitting layer, (3) light emitting
20 layer/electron transporting layer and (4) light emitting layer only. In order to enhance emission efficiency, a laminate structure consisting of light emitting layer and electron transporting layer and/or hole transporting layer is preferable.

As hole transporting material for constituting the hole
25 transporting layer, aromatic tertiary amine derivatives such as triphenylamine and oligomers or polymer thereof, or known hole transporting materials such as N-vinylcarbazole may be used. Polyparaphenylenevinylene or polydialkylfluorene can also be used. As electron transporting material for constituting the electron
30 transporting layer, known materials such as oxadiazole derivatives, triazole derivatives imidazole derivatives, triazine derivatives and organic metal complex compound as heretofore mentioned may

be used.

For the purpose of enhancing efficiency in injecting holes from anode into hole transporting layer or light emitting layer, a hole injection layer may be placed between anode and hole transporting layer or light emitting layer.

As hole injection material for constituting the hole injection layer, conductive polymers such as polythiophene derivatives, polypyrrole derivatives and polyaniline derivatives can be used. A mixture of polyethylenedioxythiophene (PEDOT) being a polythiophene derivative and polystyrenesulfonic acid (PPS) is particularly preferable for its ability to form an effective hole injection layer.

For anode, which is generally formed on a glass substrate, a light-transmitting material is used. Indium tin oxide (ITO), indium oxide, tin oxide or alloy of indium oxide and zinc oxide is preferable. Alternatively, a thin film consisting of metal such as gold, platinum and magnesium silver may be used. Conductive polymers consisting of polyaniline, polythiophene or polypyrrole, and derivatives thereof may also be used.

For anode, alkali metals such as lithium and sodium and alkali earth metals such as magnesium and calcium which have low work function are preferable from the viewpoint of electron injection property. In addition, use of stable aluminum is also preferable. For obtaining both stability and electron injection property, the layer may contain two or more materials, and such materials are disclosed in JP-A-2-15595 and JP-A-5-121172. A thin film (of about 0.01 to 100nm) of alkali metals or alkali earth metals such as cesium, barium, calcium and strontium, or alkali metal compound such as LiF and Li₂O or alkali earth metal compound such as CaF₂ and SrF₂ may be inserted between aluminum and organic layer adjacent to the cathode.

Anode and cathode can be formed by a conventional method

such as vacuum deposition method, sputtering method, ion plating method. Patterning of electrode (especially, transparent electrode) is preferably carried out by chemical etching using photolithography or physical etching using laser and the like,
5 or may be carried out with stacking masks via vacuum deposition or via sputtering.

As transparent substrate for organic EL device in the present invention, other than glass substrate which is widely used, flexible substrate of plastic or metal film may be used. In case
10 of metal film, organic or inorganic insulating layer is coated on the film before the metal film is used as substrate. Plastic material used for substrate requires excellent heat-resistance, dimensional stability, solvent-resistance, insulation property, processability, low-air-permeability and nonhygroscopic property.
15 Use of flexible material leads to provision of flexible organic EL device.

On one or both of the surface facing the electrode and the opposite surface of the substrate, moisture-impermeable layer (gas barrier layer) is preferably placed. As material for the
20 moisture-impermeable layer, inorganic materials such as silicon nitride and silicon oxide are preferably employed, and the layer can be formed by radio frequency sputtering method or the like.

Two or more transistors per organic EL (organic luminescent) pixel formed on the substrate are placed, and by addressing and
25 driving through the transistors, active-type display device can be provided. An organic transistor comprising an organic compound as its active layer enables application to a plastic substrate.

BEST MODE FOR CARRYING OUT THE INVENTION

30 Hereinafter, the present invention will be described in more detail by referring to typical examples. However, the examples are merely exemplary for the purpose of explanation and the present

invention should by no means be limited thereto.

Measurement Apparatuses used in the Examples are as follows. With respect to reagents, commercially available preparation (reagent of the highest quality) was used without purification.

5 1) ^1H -NMR

JNM EX270 manufactured by JEOL, Ltd.

270 MHz

Solvent: chloroform- d_1 or dimethyl sulfoxide- d_6

2) Elementary Analysis Equipment

10 Model CHNS-932, manufactured by LECO

3) GPC Measurement (Measurement of Molecular Weight)

Column : Shodex KF-G + KF804L + KF802 + KF801

Eluent : Tetrahydrofuran (THF)

Temperature : 40°C

15 Detector : RI (Shodex RI-71)

Example 1-1 : Synthesis of dichloromethylphenylsilane derivative
[(2-(3-((4-dichloromethylsilylphenyl)methoxy)phenyl)
pyridine)bis(2-phenylpyridine)iridium (III)]

20 By a conventional method, 2-(3-methoxyphenyl)pyridine
(hereinafter abbreviated as "3-MeO-PPy") was synthesized. That
is, as shown in the Reaction Scheme (1) below,
(3-methoxyphenyl)magnesium bromide was synthesized from 22.4 g
(120 mmol) of 3-bromoanisole with 3.4 g of magnesium (Mg) in dry
25 tetrahydrofuran (THF) in an argon stream by a conventional manner.
This was slowly added to a dry THF solution of 15.8 g (100 mmol)
of 2-bromopyridine and 1.8 g of
(1,2-bis(diphenylphosphino)-ethane)dichloronickel (II)
(Ni(dppe)Cl₂) and the mixture was stirred at 50°C for 1 hour. After
30 adding 250 ml of 5% hydrochloric acid aqueous solution to the
reaction mixture, the reaction mixture was extracted with
chloroform to obtain a target substance and the organic layer was

distilled under reduced pressure. 17.4 g (93.9 mmol) of (3-methoxyphenyl)pyridine (3-MeO-PPy) was obtained as a colorless transparent liquid. Identification was performed by $^1\text{H-NMR}$ and CHN elementary analysis.

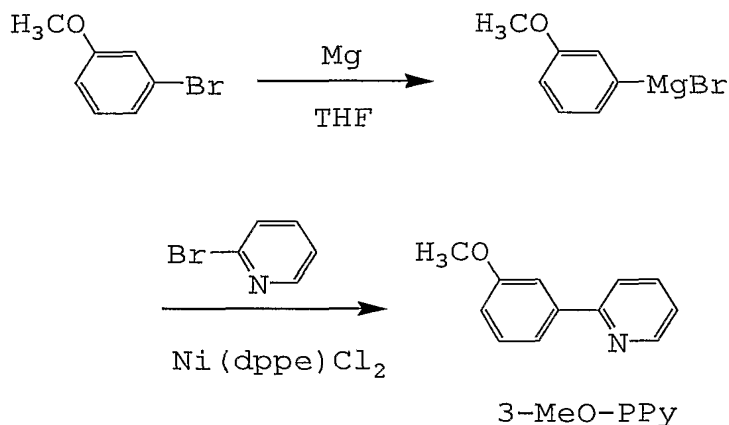
5 $^1\text{H-NMR}$ (270 MHz, CDCl_3), ppm : 8.68 (d, 1H), 7.72 (m, 2H), 7.59 (s, 1H), 7.54 (d, 1H), 7.37 (t, 1H), 7.22 (d, 1H), 6.97 (d, 1H), 3.89 (s, 3H).

Elementary analysis Calcd: C 77.81, H 5.99, N 7.56.

Found: C 77.44, H 6.01, N 7.53.

10

Reaction Scheme (1)



Then, the methoxy group of 3-MeO-PPy was hydrolyzed by a conventional method. That is, as shown in Reaction Scheme (2) below, 16.0 g (86.4 mmol) of 3-MeO-PPy was dissolved in concentrated hydrochloric acid and stirred in a sealed vessel at 130°C for 4 hours. After completion of the reaction, the reaction mixture was neutralized with an aqueous solution of sodium hydrogen carbonate and the objective compound was extracted with chloroform. Crystallization of the extract from a chloroform/hexane solution afforded 10.4 g (60.7 mmol) of 2-(3-hydroxyphenyl)pyridine

15

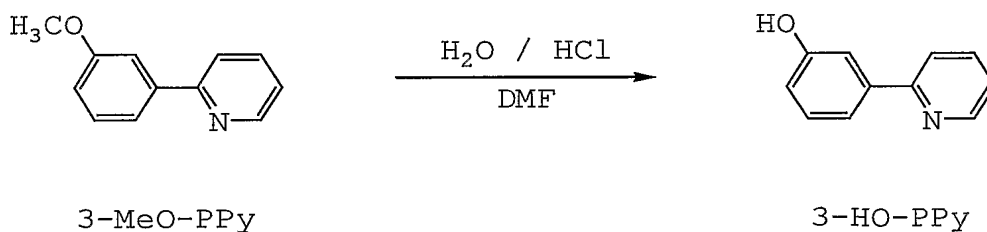
20

(hereinafter abbreviated as "3-HO-PPy") as colorless crystal. Identification was performed by ^1H -NMR and CHN elementary analysis. ^1H -NMR (270 MHz, CDCl_3), ppm : 8.66 (d, 1H), 7.76 (t, 1H), 7.67 (d, 1H), 7.56 (s, 1H), 7.40 (d, 1H), 7.30 (t, 1H), 7.26 (t, 1H), 6.88 (d, 1H), 2.08 (br, 1H).

Elementary analysis Calcd: C 77.17, H 5.30, N 8.18.

Found: C 76.81, H 5.37, N 8.11.

Reaction Scheme (2)



The hydroxyl group of 3-HO-PPy was protected by tert-butyldimethylsilyl chloride (hereinafter abbreviated as "TBDMS-Cl") by a conventional method.

That is, as shown in the Reaction Scheme (3) below, a solution of 8.6 g (50.2 mmol) of 3-HO-PPy, 10.2 g of imidazole and 11.3 g (75.0 mmol) of TBDMS-Cl in 200 ml of N,N-dimethylformamide was allowed to react at room temperature for 4 hours. Purification of the reaction mixture using a silica gel column afforded 13.0 g (45.5 mmol) of 2-(3-tert-butyldimethylsilyloxyphenyl)pyridine (hereinafter abbreviated as "3-SiO-PPy") as a colorless transparent liquid. Identification was performed by ^1H -NMR and CHN elementary analysis.

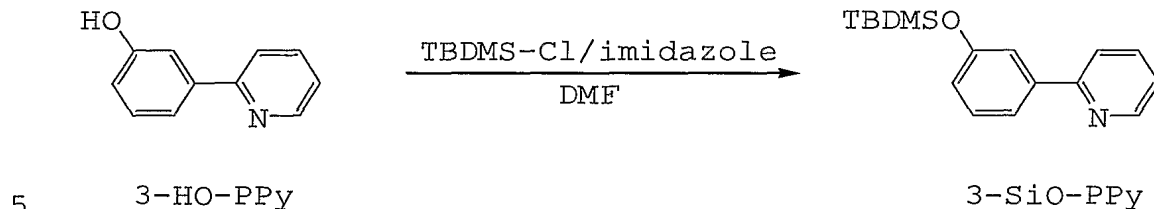
^1H -NMR (270 MHz, CDCl_3), ppm : 8.68 (d, 1H), 7.74 (t, 1H), 7.68 (d, 1H), 7.58 (d, 1H), 7.48 (s, 1H), 7.32 (t, 1H), 7.22 (t, 1H), 6.89 (d,

1H), 1.01 (s, 9H), 0.24 (s, 6H).

Elementary analysis Calcd: C 71.53, H 8.12, N 4.91.

Found: C 71.08, H 8.14, N 4.88.

Reaction Scheme (3)



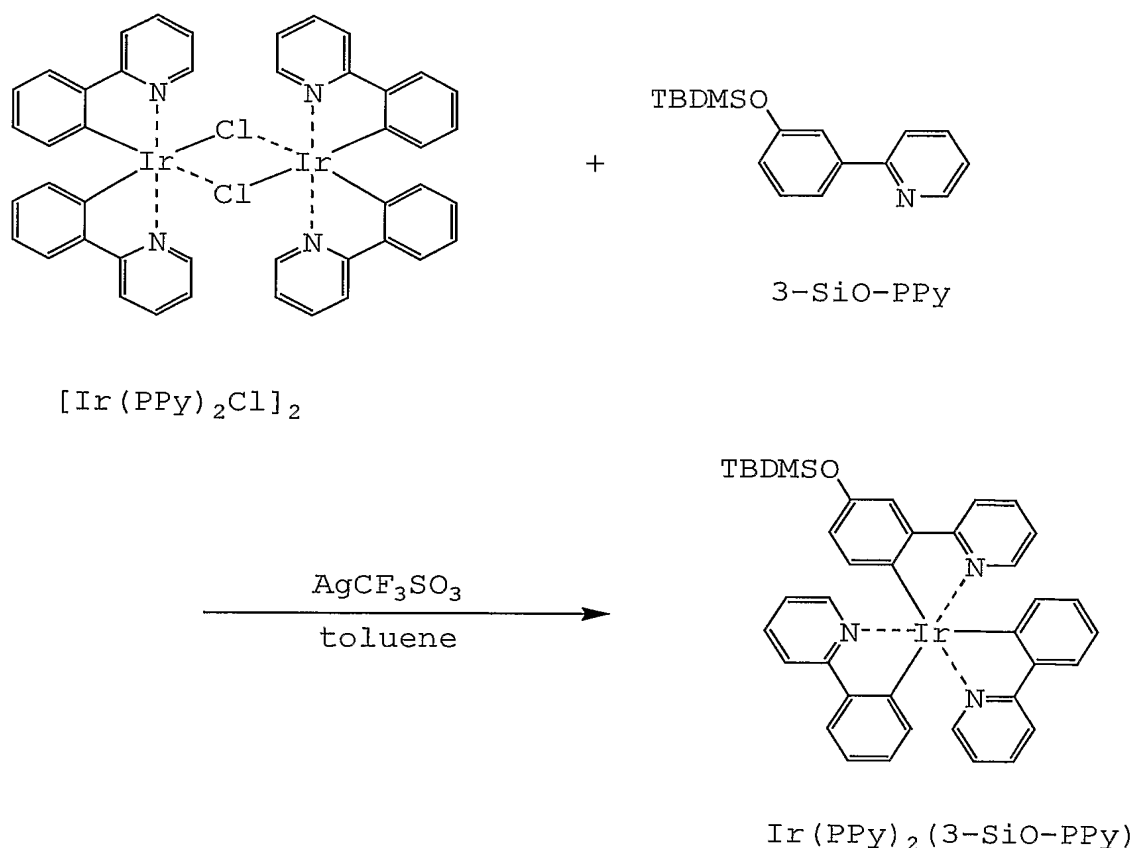
Next, the 3-SiO-PPy was allowed to react with bis(μ -chloro)tetrakis(2-phenylpyridine)diiridium (III) (hereinafter abbreviated as "[Ir(PPy)₂Cl]₂") synthesized by a conventional method in the presence of silver (I) trifluoromethanesulfonate (AgCF₃SO₃). That is, as shown in the Reaction Scheme (4) below, 2.70 g of AgCF₃SO₃ was added to a suspension of 5.71 g (20.0 mmol) of 3-SiO-PPy and 5.37 g (5.0 mmol) of [Ir(PPy)₂Cl]₂ in dry toluene and refluxed for 6 hours. Purification of the reaction mixture using a silica gel column and then distilling off the solvent afforded 2.53 g (3.2 mmol) of (2-(3-tert-butyldimethylsilyloxyphenyl)pyridine) bis(2-phenylpyridine) iridium (III) (hereinafter abbreviated as "Ir(PPy)₂(3-SiO-PPy)") as yellow powder. Identification was performed by ¹H-NMR and CHN elementary analysis.

¹H-NMR (270MHz, CDCl₃), ppm : 7.86 (d, 2H), 7.78 (d, 1H), 7.64 (d, 2H), 7.55 (m, 6H), 7.16 (s, 1H), 6.85 (m, 9H), 6.60 (d, 1H), 6.45 (d, 1H).

Elementary analysis Calcd: C 59.67, H 4.88, N 5.35.

Found: C 59.53, H 4.89, N 5.34.

Reaction Scheme (4)



Then, the silyl group of $\text{Ir}(\text{PPy})_2(3\text{-SiO-PPy})$ was hydrolyzed
 5 by a conventional method. That is, as shown in the Reaction Scheme
 (5) below, 5.1 ml of a 1 M THF solution of tetra-*n*-butylammonium
 fluoride (TBAF) was added to a THF solution of 2.00 g (2.55 mmol)
 of $\text{Ir}(\text{PPy})_2(3\text{-SiO-PPy})$ and the mixture was allowed to react at
 room temperature for 30 minutes. Purification of the reaction
 10 mixture using a silica gel column and then distilling off the solvent
 afforded 1.69 g (2.52 mmol) of (2-(3-hydroxyphenyl)pyridine)
 bis(2-phenylpyridine) iridium (III) (hereinafter abbreviated as
 " $\text{Ir}(\text{PPy})_2(3\text{-HO-PPy})$ "). Identification was performed by ^1H -NMR and
 CHN elementary analysis.

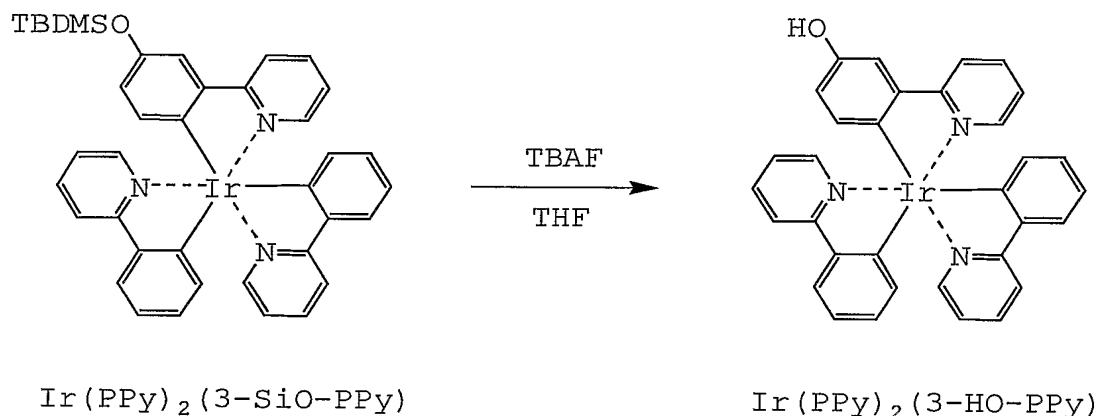
$^1\text{H-NMR}$ (270MHz, CDCl_3), ppm : 7.87 (d, 2H), 7.78 (d, 1H), 7.6 (m, 9H), 6.85 (m, 10H), 6.63 (d, 1H), 4.23 (s, 1H).

Elementary analysis Calcd: C 59.09, H 3.61, N 6.26.

Found: C 58.64, H 3.74, N 6.17.

5

Reaction Scheme (5)



Subsequently, (2-(3-((4-bromophenyl)methyloxy)phenyl)pyridine)bis(2-phenylpyridine)iridium (III) (hereinafter simply referred to as "Ir(PPy)₂(4-BrP-3-MeO-PPy)") was synthesized. That is, as shown in the Reaction Scheme (6) below, 0.34g (0.5mmol) of Ir(PPy)₂(3-HO-PPy) was dissolved in 30ml of a DMF solution having 207.3mg (1.5mmol) of K₂CO₃ dissolved therein, and further added thereto was 150mg (0.6mmol) of 4-bromobenzylbromide (BBB), followed by stirring for 8 hours at room temperature. Then, 500 ml of dilute hydrochloric acid solution and 100 ml of chloroform were added to the reaction mixture and the obtained mixture was stirred vigorously. The chloroform layer was separated and dried over magnesium sulfate and the solvent was distilled off under reduced pressure. The obtained yellow residue was dissolved in dichloromethane and the solution was subjected to silica gel column chromatography to separate a pale yellow main product. Solution

of this product was concentrated under reduced pressure and then a small amount of hexane was added thereto, followed by cooling to -20°C to obtain 282 mg (0.335 mmol) of the objective $\text{Ir}(\text{PPy})_2(4\text{-BrP-3-MeO-PPy})$ as pale yellow crystal.

5 Identification was performed by ^1H -NMR and CHN elementary analysis.

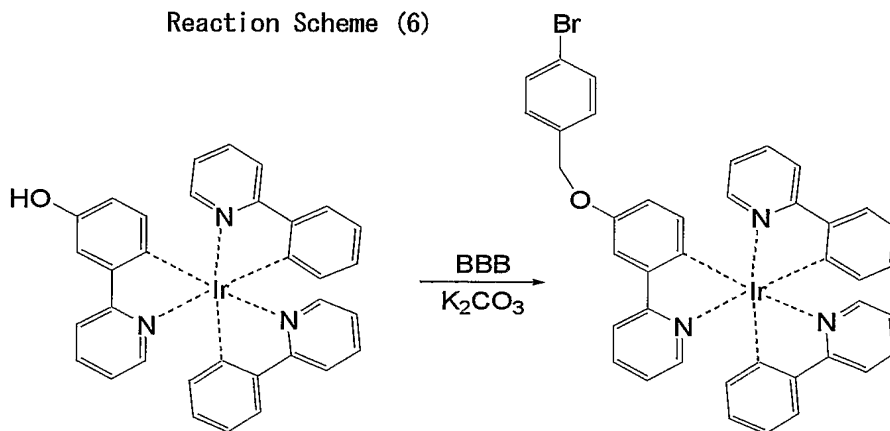
^1H -NMR (270MHz, CDCl_3), ppm : 7.86(d, 2H), 7.76(d, 1H), 7.6(m, 9H), 7.47(d, 2H), 7.21(d, 2H), 6.85(m, 10H), 6.63(d, 1H), 3.31(t, 2H).

Elementary analysis Calcd: C 57.00, H 3.83, N 4.99.

Found: C 56.86, H 3.96, N 4.91.

10

Reaction Scheme (6)



Then, (2-(3-((4-dichloromethylsilylphenyl)methoxy)phenyl)pyridine)bis(2-phenylpyridine)iridium

15 (III) (hereinafter abbreviated as " $\text{Ir}(\text{PPy})_2(4\text{-DCMPS-3-MeO-PPy})$ ") was synthesized. That is, as shown in the Reaction Scheme (7) below, a mixture of 3.6g (0.15mmol) of magnesium and 50 ml of diethyl ether was stirred well, and thereto added dropwise was 15ml of a diethyl ether solution having 114mg (0.135mmol) of

20 $\text{Ir}(\text{PPy})_2(4\text{-BrP-3-MeO-PPy})$ dissolved therein, followed by stirring for 12 hours. Subsequently dropped thereto over 2 hours was 100ml of a diethyl ether solution having 149mg (1mmol) of methyltrichlorosilane dissolved therein. After completion of the dropping, the mixture was refluxed for 12 hours and cooled,

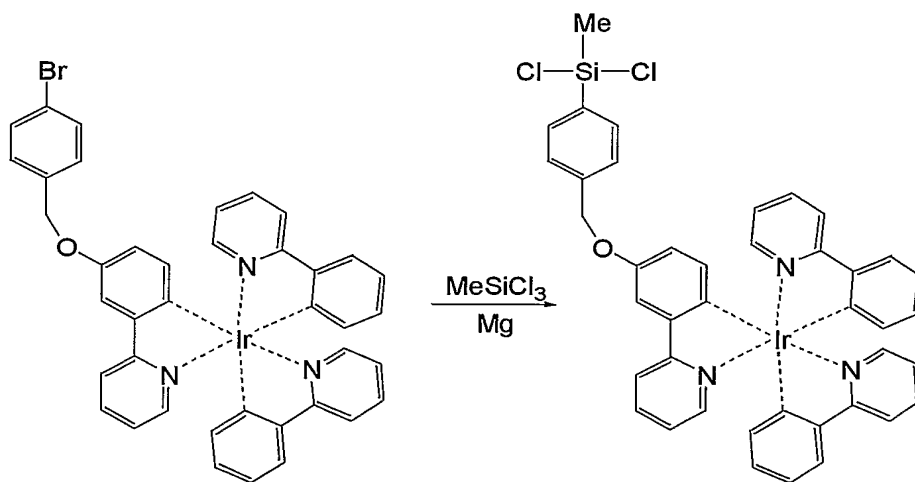
200ml of hexane was added to filter out purified salt, and the filtrate was concentrated by a rotary evaporator. The obtained solid substance was dissolved in a small amount of dichloromethane and charged in silica gel column chromatography, followed by flowing dichloromethane therethrough to remove eluted impurities. Subsequently, flowing a dichloromethane/ethyl acetate mixed solvent resulted in elution of a pale yellow complex, which was recovered and dried under reduced pressure, followed by recrystallization of the residue from dichloromethane/hexane mixed solution at -20°C to obtain 57 mg (0.065mmol) of $\text{Ir}(\text{PPy})_2(4\text{-DCMPS-3-MeO-PPy})$ as pale yellow solid. Identification was performed by $^1\text{H-NMR}$ and CHN elementary analysis.

$^1\text{H-NMR}$ (270MHz, CDCl_3), ppm : 7.86 (d, 2H), 7.76 (d, 1H), 7.6 (m, 9H), 7.46 (d, 2H), 7.22 (d, 2H), 6.85 (m, 10H), 6.63 (d, 1H), 3.31 (t, 2H).

Elementary analysis Calcd: C 56.16, H 4.02, N 4.79.

Found: C 56.25, H 3.93, N 4.77.

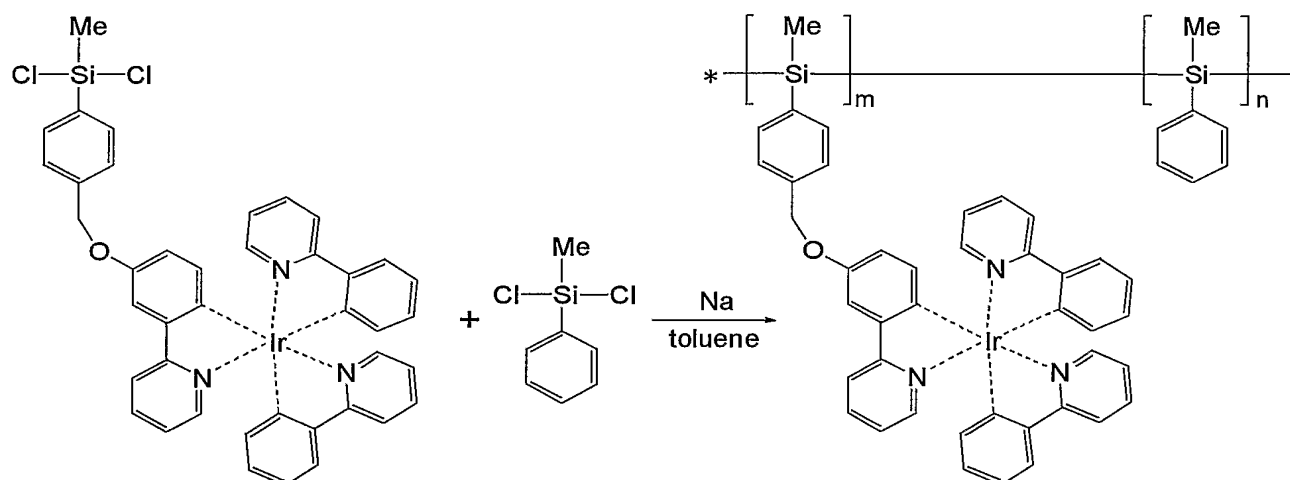
Reaction Scheme (7)



Example 1-2: Polymerization of $\text{Ir}(\text{PPy})_2(4\text{-DCMPS-3-MeO-PPy})$ /dichloromethylphenylsilane(DCMPS) copolymer

Copolymer of $\text{Ir}(\text{PPy})_2(4\text{-DCMPS-3-MeO-PPy})$ and DCMPS was
5 polymerized by a conventional method. That is, as shown in the
Reaction Scheme(8) below, a mixture of 230mg (10mmol) of sodium
and 20ml of toluene was heated to reflux and well stirred. Thereto
dropped was 10 ml of a toluene solution having 35mg (0.04mmol)
of $\text{Ir}(\text{PPy})_2(4\text{-DCMPS-3-MeO-PPy})$ and 765mg (4mmol) of DCMPS
10 dissolved therein. After completion of the dropping, the mixture
was refluxed for 60 hours and cooled, a mixed solution of 20 ml
of hexane and 20ml of methanol was added and stirred for 1 hour.
Then, 100 ml of dilute hydrochloric acid solution was added to
the reaction mixture, the solvent layer was separated and dried
15 over magnesium sulfate and the solvent was distilled off under
reduced pressure. The obtained pale yellow residue was washed
in acetone and vacuum-dried to obtain a target copolymer 58mg.
Identification of the product was performed by Ir elementary
analysis and GPC measurements.
20 Elementary analysis: Ir 0.06,
GPC(THF, polystyrene standard):Mw 9800, Mw/Mn=2.11.

Reaction Scheme (8)



5

Example 1-3:

First, the phosphorescent polysilane obtained in Example 1-2 was dissolved in dichloroethane to prepare a 1 mass% solution. On an ITO-coated glass substrate treated in organic rinse and UV ozone was formed a light emitting layer having a thickness of 100nm by a spin coating method at a spin speed of 1,000 rpm. This was sufficiently vacuum-dried, and 30 nm calcium and 100nm aluminum were formed by vacuum deposition method. By using glass and UV-curable resin, the device was sealed in a glove box filled with high-purity nitrogen gas. When positive voltage of 10V was applied to the ITO side of the organic EL device and negative voltage of 10V to the aluminum side of the organic EL device, green luminescence having a peak wave-length of 520nm was observed. By the shape of luminescence spectrum, it was confirmed that the luminescence was emitted from phosphorescent units. The external quantum efficiency in luminescence was approximately 2%.

Example 2-1 : Synthesis of dichloromethylphenylsilane derivative

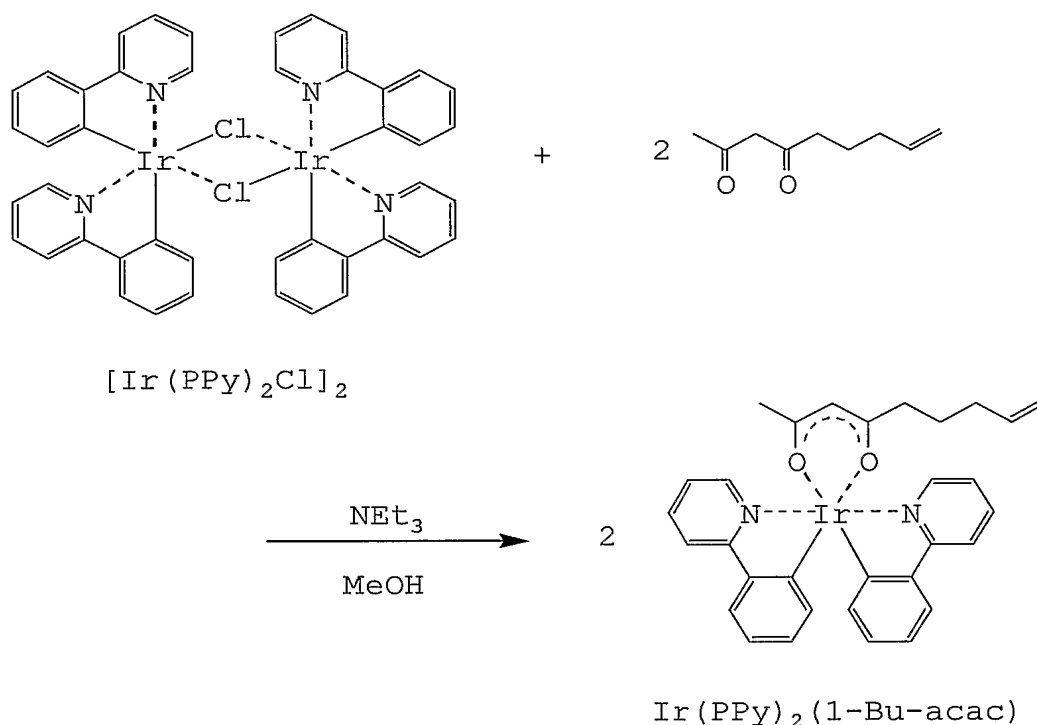
[9-(4-dichloromethylsilylphenyl)methoxy]nonan-2,4-dionate)
bis(2-phenylpyridine) Iridium (III)]

As shown in the Reaction Scheme (9) below,
di(μ -chloro)tetrakis(2-phenylpyridine) diiridium (III)
5 (hereinafter abbreviated as "[Ir(PPy)₂Cl]₂") synthesized by a
conventional method and 8-nonen-2,4-dione synthesized by a known
method (H. Gerlach et al., *Helv. Chim. Acta*, 60, 638 (1977)) were
allowed to react to synthesize
(8-nonen-2,4-dionate)bis(2-phenylpyridine)iridium(III)
10 (hereinafter abbreviated as "Ir(PPy)₂(1-Bu-acac)"). That is, 261
mg (0.24 mmol) of [Ir(PPy)₂Cl]₂ was suspended in 30 ml of methanol
degassed by nitrogen gas and 87 mg (0.56 mmol) of 8-nonen-2,4-dione
and 756 mg (0.75 mmol) of triethylamine (NEt₃) were added thereto,
and the obtained mixture was heated to reflux in an oil bath for
15 3 hours. The obtained pale yellow liquid reaction mixture was
cooled to room temperature and concentrated by using a rotary
evaporator. Then, 200 ml of dilute hydrochloric acid solution
and 50 ml of chloroform were added to the reaction mixture and
the obtained mixture was stirred vigorously. The chloroform layer
20 was separated and dried over magnesium sulfate and the solvent
was distilled off under reduced pressure. The obtained yellow
residue was dissolved in dichloromethane and the solution was
subjected to silica gel column chromatography to separate a pale
yellow main product. Solution of the product was concentrated
25 under reduced pressure and then a small amount of hexane was added
thereto, followed by cooling to -20°C to obtain 270 mg (0.41 mmol)
of the objective Ir(PPy)₂(1-Bu-acac) as pale yellow crystal.
Identification was performed by ¹H-NMR and CHN elementary analysis.
¹H-NMR (270 MHz, CDCl₃), ppm : 8.49 (d, 2H), 7.83 (t, 2H), 7.70 (m,
30 2H), 7.54 (t, 2H), 7.10 (m, 2H), 6.80 (t, 2H), 6.68 (m, 2H), 6.35
(d, 1H), 6.25 (d, 1H), 5.61 (m, 1H), 5.19 (s, 1H), 4.86 (m, 2H),
1.99 (t, 2H), 1.79 (s, 3H), 1.72 (m, 2H), 1.38 (m, 2H).

Elementary analysis Calcd: C 56.95; H 4.47, N 4.28.

Found: C 55.84, H 4.32, N 3.97.

Reaction Scheme (9)



5

Next, (9-hydroxy-2,4-nonandionate)bis(2-phenylpyridine) iridium (hereinafter abbreviated as " $\text{Ir}(\text{PPy})_2[1\text{-(OH-Bu)-acac}]$ ") was synthesized. That is, as shown in the Reaction Scheme (10) below, to a solution of 167 mg (0.26 mmol) of $\text{Ir}(\text{PPy})_2(1\text{-Bu-acac})$ in 10 ml of THF was dripped 1.0 ml (0.5 mmol) of a 0.5 M THF solution of 9-borabicyclo[3.3.1]nonane (hereinafter abbreviated as 9-BBN) and the solution was heated to reflux for 25 minutes. Then, to the reaction mixture were added 0.2 ml (0.60 mmol) of a 3M aqueous NaOH solution and 0.060 ml (0.62 mmol) of a 35% H_2O_2 solution in the order cited, and the mixture was stirred at room temperature for 12 hours. Then, 20 ml of water was added thereto and the mixture

10

15

was concentrated by using a rotary evaporator. After adding chloroform and well shaking, the organic layer was concentrated to dryness under reduced pressure. The obtained yellow solid was dissolved in a small amount of dichloromethane and the solution

5 was charged in a silica gel column followed by flowing dichloromethane therethrough to remove eluted impurities. Subsequently, flowing a dichloromethane/ethyl acetate mixed solvent of 1:1 (by volume ratio) resulted in elution of a pale yellow complex, which was recovered and dried under reduced

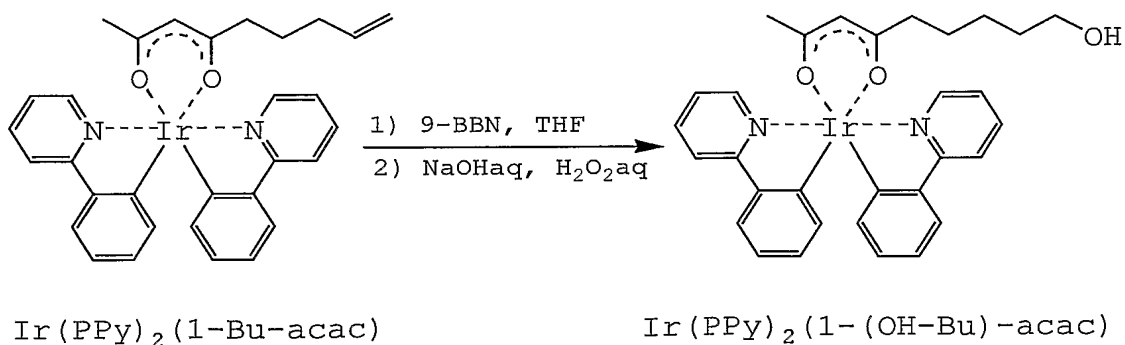
10 pressure, followed by recrystallization of the residue from dichloromethane/hexane mixed solution at -20°C to obtain 23 mg (0.034 mmol) of $\text{Ir}(\text{PPy})_2[1-(\text{OH-Bu})\text{-acac}]$ as pale yellow solid. Identification was performed by $^1\text{H-NMR}$ and CHN elementary analysis.

$^1\text{H-NMR}$ (270 MHz, CDCl_3), ppm : 8.50 (d, 2H), 7.82 (t, 2H), 7.72 (t, 2H), 7.55 (t, 2H), 7.12 (t, 2H), 6.81 (t, 2H), 6.69 (t, 2H), 6.31 (d, 1H), 6.26 (d, 1H), 5.19 (s, 1H), 3.44 (t, 2H), 1.98 (t, 2H), 1.79 (s, 3H), 1.34 (m, 4H), 1.05 (m, 2H).

Elementary analysis Calcd: C 55.42, H 4.65, N 4.17.
Found: C 55.76, H 4.71, N 4.19.

20

Reaction Scheme (10)



Then, (9-(4-bromophenyl)methoxy-2,4-nonandionate) bis(2-phenylpyridine)iridium (hereinafter abbreviated as

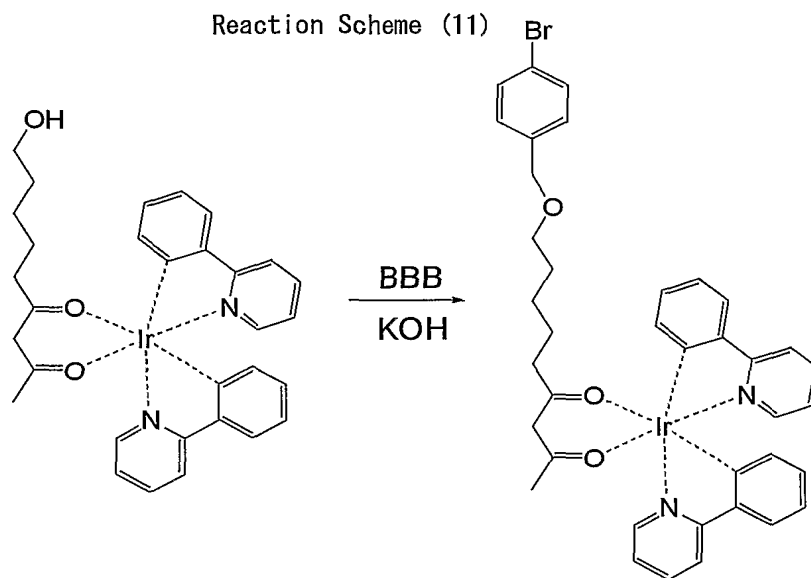
25 " $\text{Ir}(\text{PPy})_2[4\text{-BrP-Meo-acac}]$ ") was synthesized. That is, as shown

in the Reaction Scheme (11) below, 114mg (0.169mmol) of $\text{Ir}(\text{PPy})_2[1-(\text{OH}-\text{Bu})-\text{acac}]$ was dissolved in a 10 ml DMSO solution having 28 mg (0.5 mmol) of KOH dissolved therein, and further to this solution was added 50mg (0.2mmol) of BBB, followed by stirring for 6 hours at room temperature. Then, 200 ml of dilute hydrochloric acid solution and 50 ml of chloroform were added to the reaction mixture and the obtained mixture was stirred vigorously. The chloroform layer was separated and dried over magnesium sulfate and the solvent was distilled off under reduced pressure. The obtained yellow residue was dissolved in dichloromethane and the solution was subjected to silica gel column chromatography with the dichloromethane as eluent to separate a pale yellow main product. A solution of this product was concentrated under reduced pressure and then a small amount of hexane was added thereto, followed by cooling to -20°C to obtain 114 mg (0.135 mmol) of the objective $\text{Ir}(\text{PPy})_2[4-\text{BrP}-\text{MeO}-\text{acac}]$ as pale yellow crystal. Identification was performed by ^1H -NMR and CHN elementary analysis.

^1H -NMR (270MHz, CDCl_3), ppm : 8.50 (d, 2H), 7.82 (t, 2H), 7.72 (t, 2H), 7.55 (t, 2H), 7.47 (d, 2H), 7.21 (d, 2H), 7.12 (t, 2H), 6.81 (t, 2H), 6.69 (t, 2H), 6.31 (d, 1H), 6.26 (d, 1H), 5.19 (s, 1H), 4.40 (s, 2H), 3.31 (t, 2H), 1.98 (t, 2H), 1.79 (s, 3H), 1.34 (m, 2H), 1.22 (m, 2H), 1.04 (m, 2H).

Elementary analysis Calcd: C 54.09; H 4.46, N 3.32.

Found: C 54.24, H 4.78, N 3.35.



Subsequently, (9-(4-dichloromethylsilylphenyl) methoxy-2,4-nonandionate)bis(2-phenylpyridine) iridium

5 (hereinafter abbreviated as "Ir(PPy)₂[4-DCMPS-3-MeO-acac]") was synthesized. That is, as shown in the Reaction Scheme (12) below, a mixture of 3.6g (0.15mmol) of magnesium and 50 ml of diethyl ether was stirred well, and thereto dropped was 10ml of a diethyl ether solution having 114mg (0.135mmol) of

10 Ir(PPy)₂(4-BrP-MeO-acac) dissolved therein, followed by stirring for 12 hours. Subsequently dropped thereto over 2 hours was 100ml of a diethyl ether solution having 149mg (1mmol) of methyltrichlorosilane dissolved therein. After completion of the dropping, the mixture was refluxed for 12 hours and cooled, 200ml

15 of hexane was added to filter out purified salt, and the filtrate was concentrated by a rotary evaporator. The obtained solid substance was dissolved in a small amount of dichloromethane and charged in silica gel column chromatography, followed by flowing dichloromethane therethrough to remove eluted impurities.

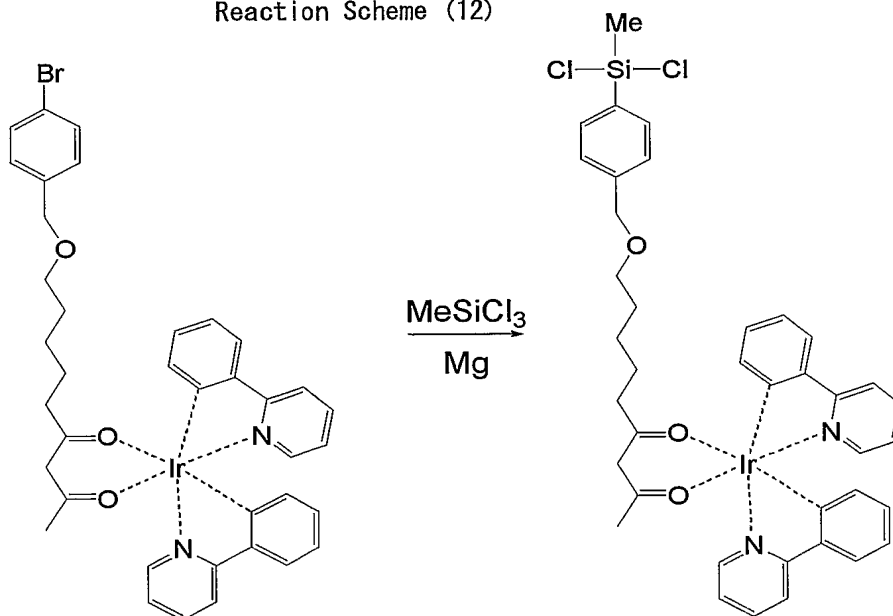
20 Subsequently, flowing a dichloromethane/ethyl acetate mixed solvent resulted in elution of a pale yellow complex, which was recovered and dried under reduced pressure, followed by

recrystallization of the residue from dichloromethane/hexane mixed solution at -20°C to obtain 77 mg (0.088mmol) of $\text{Ir}(\text{PPy})_2(4\text{-DCMPS-3-MeO-acac})$ as pale yellow solid. Identification was performed by $^1\text{H-NMR}$ and CHN elementary analysis.

5 $^1\text{H-NMR}$ (270MHz, CDCl_3), ppm : 8.50 (d, 2H), 7.82 (t, 2H), 7.72 (t, 2H), 7.55 (t, 2H), 7.46 (d, 2H), 7.22 (d, 2H), 7.12 (t, 2H), 6.81 (t, 2H), 6.69 (t, 2H), 6.31 (d, 1H), 6.26 (d, 1H), 5.19 (s, 1H), 4.40 (s, 2H), 3.31 (t, 2H), 1.98 (t, 2H), 1.79 (s, 3H), 1.34 (m, 2H), 1.22 (m, 2H), 1.04 (m, 2H).

10 Elementary analysis Calcd: C 53.35; H 4.82, N 3.19.
Found: C 53.44, H 4.91, N 3.31.

Reaction Scheme (12)



15 Example 2-2 : Polymerization of $\text{Ir}(\text{PPy})_2[4\text{-DCMPS-MeO-acac}]$ / dichloromethylphenylsilane(DCMPS) copolymer

As shown in the Reaction Scheme (13) below, copolymer of $\text{Ir}(\text{PPy})_2[4\text{-DCMPS-MeO-acac}]$ and DCMPS was polymerized. That is, a mixture of 230mg (10mmol) of sodium and 20ml of toluene was heated to reflux and well stirred. Thereto dropped was 10 ml of a toluene

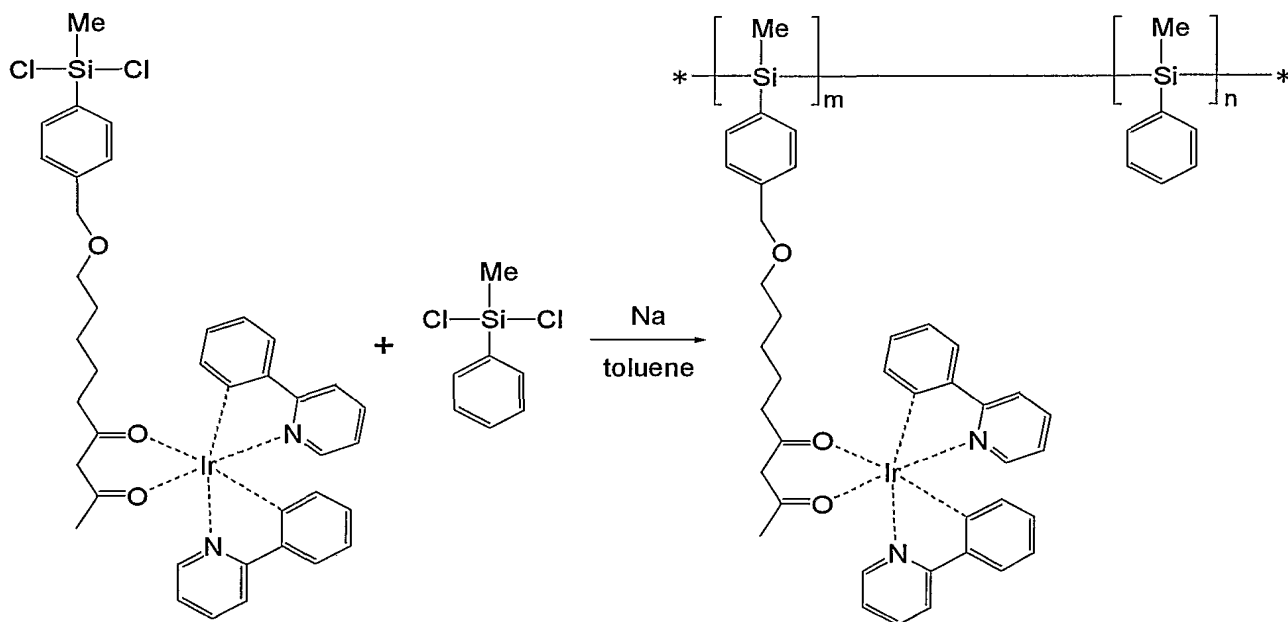
20

solution having 32mg (0.04mmol) of $\text{Ir}(\text{PPy})_2[4\text{-DCMPS-MeO-acac}]$ and 765mg (4mmol) of DCMPS dissolved therein. After completion of the dropping, the mixture was refluxed for 60 hours and cooled, a mixed solution of 20 ml of hexane and 20ml of methanol was added and stirred for 1 hour. Then, 100 ml of dilute hydrochloric acid solution was added to the reaction mixture, the solvent layer was separated and dried over magnesium sulfate and the solvent was distilled off under reduced pressure. The obtained yellow residue was washed in acetone and vacuum-dried to obtain a target copolymer 66mg. Identification of the product was performed by Ir elementary analysis and GPC measurements.

Elementary analysis: Ir 0.04,

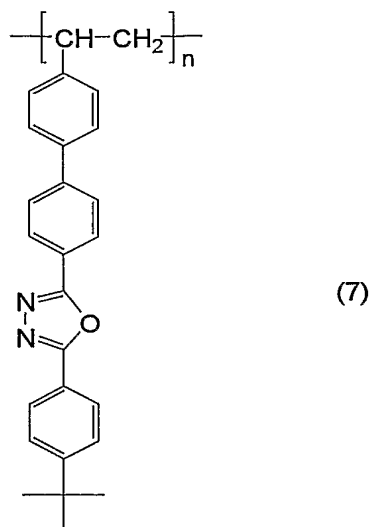
GPC(THF, polystyrene standard): M_w 10800, $M_w/M_n=1.89$.

Reaction Scheme (13)



Example 2-3 :

For the purpose of enhancing electron transporting property of light emitting layer and facilitating hole injection into light-emitting layer, a conductive polymer layer was inserted and electron transporting compound was mixed into the light emitting layer. First, on an ITO-coated glass substrate, conductive polymer layer of PEDT/PPS was formed to a thickness of 50nm by a spin coating method and dried at about 180°C. Secondly, 70 mass% of the phosphorescent polysilane obtained in Example 2-2 and 30 mass% of an electron transporting polymer, poly-PBD, synthesized by a method disclosed in JP-A-10-1665 and represented by formula (7) below, were dissolved in dichloroethane to prepare a solution (1 mass%). Using this solution, a film having a thickness of 100nm was formed on the PEDT/PPS layer and vacuum-dried sufficiently. Finally formed thereon was calcium having a thickness of 30nm and aluminum having a thickness of 100nm. After sealing the resulted device, its properties were measured. When a 5V positive voltage was applied to the ITO side of the organic EL device and a 5V negative voltage to the aluminum side of the device, green luminescence having a peak wave length of 520 nm and a luminance of 200 cd/m² was observed. It was confirmed that the luminescence was emitted from a phosphorescent-light emitting unit. The value measured as the external quantum efficiency was 6%, which exceeds the value of a conventional fluorescent polymer EL device.



Example 3-1 : Synthesis of dichloromethylsilane derivative
 [(5-(4-dichloromethylsilylphenyl)methyloxymethyl)-picolinato]
 bis(2-(2,4-difluorophenyl)pyridine)iridium (III)

5 As shown in the Reaction Scheme (14) below,
 2-(2,4-difluorophenyl)pyridine (hereinafter abbreviated as
 "2,4-F-PPy") was synthesized by a conventional method. That is,
 under argon stream, 8.69 g (55.0 mmol) of 2-bromopyridine was
 dissolved in 200 ml of dry tetrahydrofuran and cooled to -78°C.
 10 To this was dripped 38.7 ml (61.9 mmol) of a 1.6 M hexane solution
 of n-butyllithium over 30 minutes. After completion of the
 dripping, further a solution of 7.5 g (55.0 mmol) of zinc chloride
 in 50 ml of dry tetrahydrofuran was dripped over 30 minutes. After
 completion of the dripping, the temperature of the mixture was
 15 slowly elevated to 0°C and 9.65 g (55.0 mmol) of
 1-bromo-2,4-difluorobenzene and 2.31 g (2.0 mmol) of
 tetrakis(triphenylphosphine)palladium (0) were added thereto.
 The mixture was stirred for 6 hours under reflux and then 200 ml
 of saturated saline was added to the reaction mixture, followed
 20 by extraction of the reaction mixture with diethyl ether. After
 drying the extract, concentration and purification by column
 chromatography (silica gel; chloroform/hexane) afforded 6.00 g

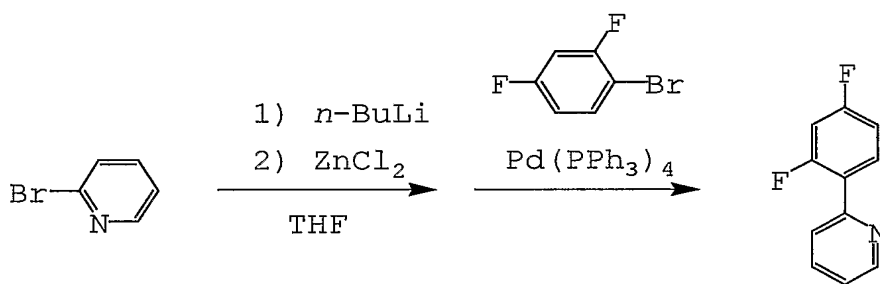
(31.4 mmol) of 2,4-F-PPy colorless transparent oil. Identification was performed by elementary analysis of ^1H -NMR and CHN elementary analysis.

^1H -NMR (270MHz, CDCl_3), ppm : 8.71 (d, 1H), 8.00 (td, 1H), 7.8-7.7 (m, 2H), 7.3-7.2 (1H), 7.1-6.8 (m, 2H).

Elementary analysis Calcd: C 69.11, H 3.69, N 7.33.

Found: C 68.98, H 3.80, N 7.31.

Reaction Scheme (14)



10

Subsequently, as shown in the Reaction Scheme (15) below, bis (μ -chloro) tetrakis[2-(2,4-difluorophenyl)pyridine] diiridium (III) (hereinafter abbreviated as "[Ir(2,4-F-PPy) $_2\text{Cl}$] $_2$ ") was synthesized by reacting 2,4-F-PPy with sodium hexachloroiridate n-hydrate. That is, 0.96 g (5.0 mmol) of 2,4-F-PPy and 1.00 g of sodium hexachloroiridate n-hydrate were dissolved in 40 ml of a 3:1 mixed solvent of 2-ethoxyethanol and water (by volume ratio) and argon gas was blown therein for 30 minutes and the mixture was stirred for 5 hours under reflux. The formed precipitate was collected by filtration and washed with ethanol and then with a small amount of acetone, followed by drying in vacuum for 5 hours to obtain 0.79 g (0.65 mmol) of the objective [Ir(2,4-F-PPy) $_2\text{Cl}$] $_2$ as yellow powder. Identification was performed by ^1H -NMR and CHN elementary analysis.

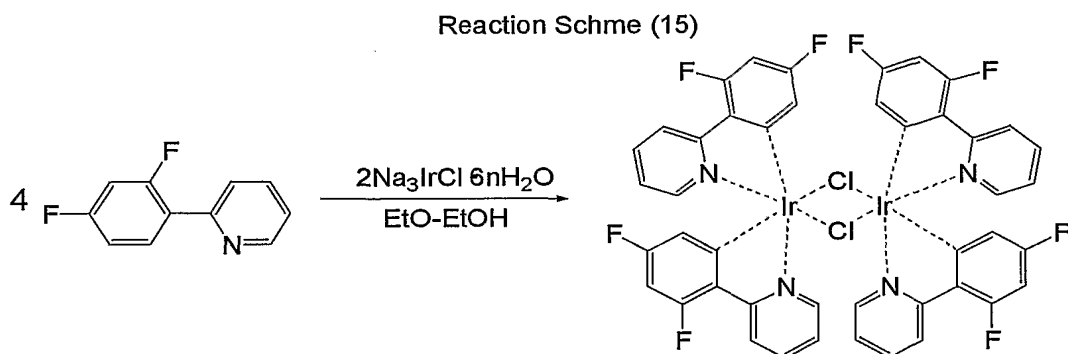
25

$^1\text{H-NMR}$ (270MHz, CDCl_3), ppm : 9.12 (d, 4H), 8.31 (d, 4H), 7.83 (dd, 4H), 6.82 (dd, 4H), 6.34 (ddd, 4H), 5.29 (dd, 4H).

Elementary analysis Calcd: C 43.46, H 1.99, N 4.61.

Found: C 43.39, H 2.03, N 4.55.

5

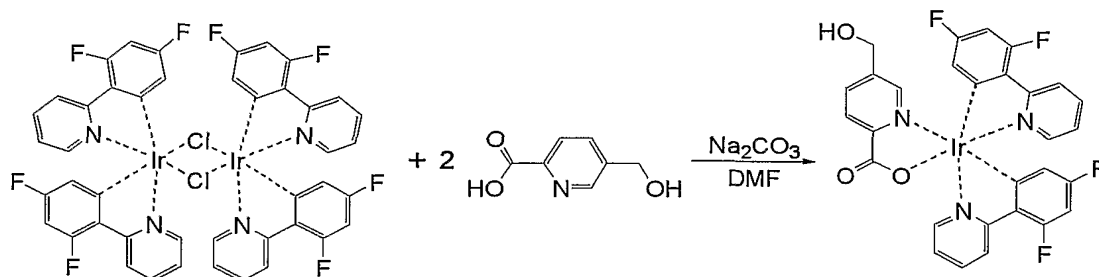


Then, (5-(hydroxymethyl)picolinato) bis (2-(2,4-difluorophenyl)pyridinate) iridium (III) (hereinafter abbreviated as "Ir(2,4-F-PPy)₂(5-HO-pic)") was synthesized. That is, as shown in the Reaction Scheme (16) below, 10 ml of dry N,N-dimethylformamide (DMF) was added to a mixture of 121.6 mg (0.1 mmol) of [Ir(2,4-F-PPy)₂Cl]₂, 45.9 mg (0.3 mmol) of 5-hydroxymethylpicolinic acid, and 106.0 mg (1.0 mmol) of sodium carbonate under argon stream and the mixture was stirred at 80°C for 2 hours. After adding 50 ml of water, the reaction mixture was extracted with ethyl acetate. After drying the obtained solution over magnesium sulfate, it was concentrated and purified by column chromatography (silica gel, methanol : chloroform = 1:19 (by volume ratio)). Recrystallization from hexane/chloroform afforded 108.7 mg of Ir(2,4-F-PPy)₂(5-HO-pic) as yellow crystal. Identification was performed by $^1\text{H-NMR}$ and CHN elementary analysis. $^1\text{H-NMR}$ (270MHz, DMSO-d_6), ppm : 8.54 (d, 1H), 8.3-8.2 (m, 2H), 8.1-8.0 (m, 4H), 7.70 (s, 1H), 7.61 (d, 1H), 7.49 (dd, 1H), 7.32 (dd, 1H), 6.9-6.7 (m, 2H), 5.71 (dd, 1H), 5.46 (dd, 1H), 5.42 (t, 1H), 4.49 (d, 2H).

Elementary analysis Calcd: C 48.06, H 2.50, N 5.80.

Found: C 48.05, H 2.54, N 5.86.

Reaction Scheme(16)



5

Next, (5-(4-bromophenylmethyloxymethyl)picolinato) bis(2-(2,4-difluorophenyl)pyridinate)iridium (III) (hereinafter abbreviated as "Ir(2,4-F-PPy)₂(4-BrP-MeO-pic)") was synthesized. That is, as shown in the Reaction Scheme (17) below, 0.11g (0.15mmol) of Ir(2,4-F-PPy)₂(5-HO-pic) was dissolved in a 10 ml DMSO solution having 28 mg (0.5 mmol) of KOH dissolved therein, and further to this solution was added 50mg (0.2mmol) of BBB, followed by stirring for 8 hours at room temperature. Then, 200 ml of dilute hydrochloric acid solution and 50 ml of chloroform were added to the reaction mixture and the obtained mixture was stirred vigorously. The chloroform layer was separated and dried over magnesium sulfate and the solvent was distilled off under reduced pressure. The obtained yellow residue was dissolved in dichloromethane and the solution was subjected to silica gel column chromatography with the dichloromethane as eluent to separate a pale yellow main product. Solution of this product was concentrated under reduced pressure and then a small amount of hexane was added thereto, followed by cooling to -20°C to obtain 44.8 mg (0.05 mmol) of the objective Ir(2,4-F-PPy)₂(4-BrP-MeO-pic) as pale yellow crystal. Identification was performed by ¹H-NMR and CHN elementary

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25

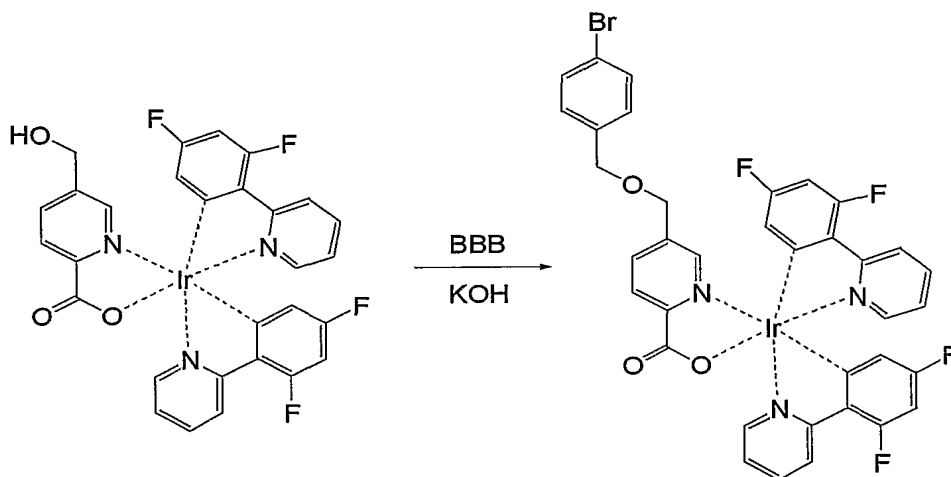
analysis.

$^1\text{H-NMR}$ (270MHz, DMSO-d_6), ppm: 8.54 (d, 1H), 8.3–8.2 (m, 2H), 8.1–8.0 (m, 4H), 7.70 (s, 1H), 7.61 (d, 1H), 7.49 (dd, 1H), 7.47 (m, 2H), 7.21 (m, 2H), 7.32 (dd, 1H), 6.9–6.7 (m, 2H), 5.71 (dd, 1H), 5.46 (dd, 1H), 4.90 (s, 2H), 3.11 (s, 2H).

Elementary analysis Calcd: C 48.22, H 2.92, N 4.69.

Found: C 48.18, H 2.94, N 4.73.

Reaction Scheme (17)



Then, (5-(4-dichloromethylsilylphenylmethyloxymethyl) picoilinato)bis(2-(2,4-difluorophenyl)pyridinate)iridium (III) (hereinafter abbreviated as "Ir(2,4-F-PPy)₂(4-DCMPS-MeO-Pic)") was synthesized. That is, as shown in the Reaction Scheme (18) below, a mixture of 3.6g (0.15mmol) of magnesium and 50ml of diethyl ether was stirred well, and thereto added dropwise was 15ml of a diethyl ether solution having 114mg (0.135mmol) of Ir(2,4-F-PPy)₂(4-BrP-MeO-pic) dissolved therein, followed by stirring for 12 hours. Further dropped thereto over 2 hours was 100ml of a diethyl ether solution having 149mg (1mmol) of methyltrichlorosilane dissolved therein. After completion of the

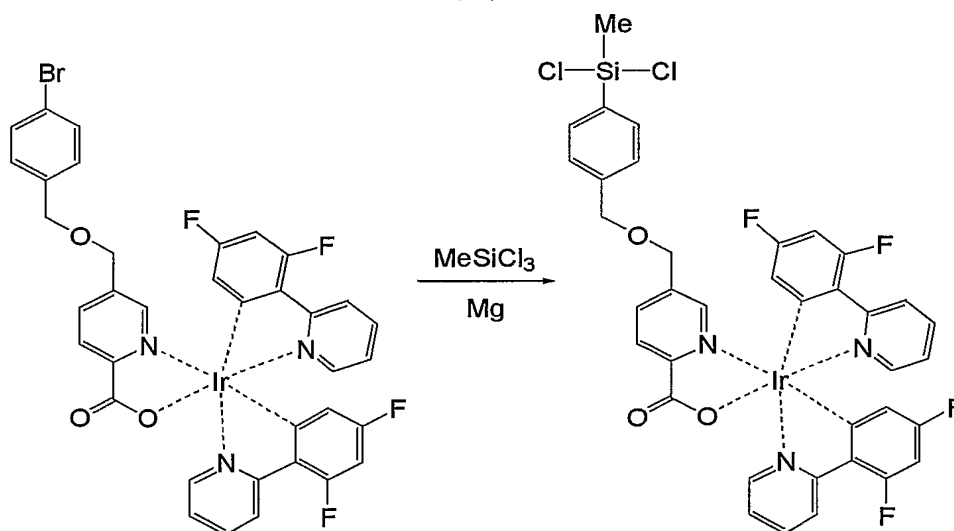
dropping, the mixture was refluxed for 12 hours and cooled, 200ml of hexane was added to filter out purified salt, and the filtrate was condensed by a rotary evaporator. The obtained solid substance was dissolved in a small amount of dichloromethane and charged in silica gel column chromatography, followed by flowing dichloromethane therethrough to remove eluted impurities. Subsequently, flowing a dichloromethane/ethyl acetate mixed solvent resulted in elution of a pale yellow complex, which was recovered and dried under reduced pressure, followed by recrystallization of the residue from dichloromethane/hexane mixed solution at -20°C to obtain 57 mg (0.065mmol) of $\text{Ir}(2,4\text{-F-PPy})_2(4\text{-DCMPS-MeO-pic})$ as pale yellow solid. Identification was performed by $^1\text{H-NMR}$ and CHN elementary analysis.

$^1\text{H-NMR}$ (270MHz, DMSO-d_6), ppm: 8.54 (d, 1H), 8.3-8.2 (m, 2H), 8.1-8.0 (m, 4H), 7.70 (s, 1H), 7.61 (d, 1H), 7.49 (dd, 2H), 7.46 (m, 2H), 7.22 (m, 2H), 7.32 (dd, 1H), 6.9-6.7 (m, 2H), 5.71 (dd, 1H), 5.46 (dd, 1H), 4.90 (s, 2H), 3.11 (s, 2H).

Elementary analysis Calcd: C 47.74, H 3.14, N 4.51.

Found: C 47.81, H 3.11, N 4.48.

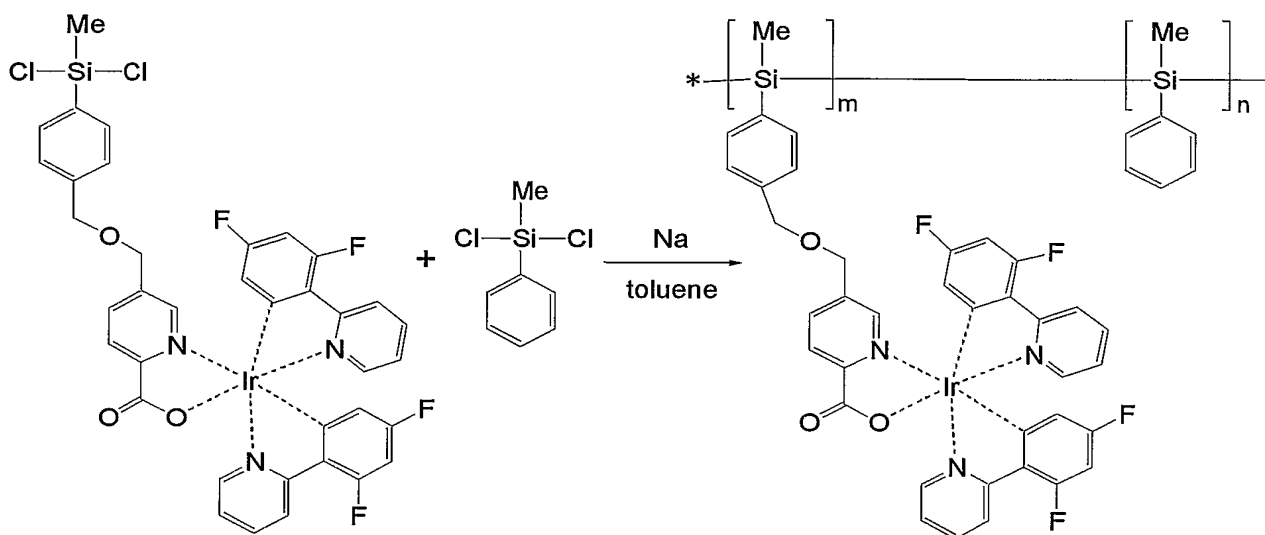
Reaction Scheme (18)



Example 3-2: Polymerization of copolymer of
Ir(2,4-F-PPy)₂(4-DCMPS-MeO-pic)/DCMPS

Copolymer of Ir(2,4-F-PPy)₂(4-DCMPS-MeO-pic) and DCMPS was
5 polymerized. That is, as shown in Reaction Scheme (19) below,
a mixture of 230mg (10mmol) of sodium and 20ml of toluene was heated
to reflux and well stirred. Thereto dropped was 10 ml of a toluene
solution having 35mg (0.04mmol) of
Ir(2,4-F-PPy)₂(4-DCMPS-MeO-pic) and 765mg (4mmol) of DCMPS
10 dissolved therein. After completion of the dropping, the mixture
was refluxed for 60 hours and cooled, a mixed solution of 20 ml
of hexane and 20ml of methanol was added and stirred for 1 hour.
Then, 100 ml of dilute hydrochloric acid solution was added to
the reaction mixture, the solvent layer was separated and dried
15 over magnesium sulfate and the solvent was distilled off under
reduced pressure. The obtained yellow residue was washed in
acetone and vacuum-dried to obtain a target copolymer 73mg.
Identification of the product was performed by Ir elementary
analysis and GPC measurements.
20 Elementary analysis: Ir 0.03,
GPC(THF, polystyrene standard):Mw 8900, Mw/Mn=2.45.

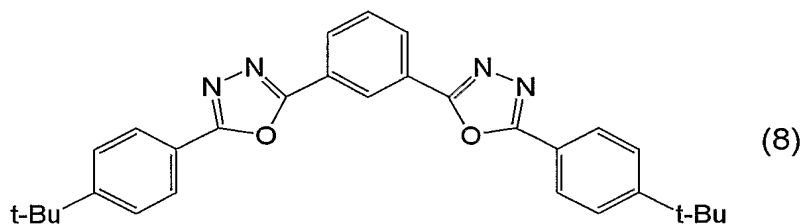
Reaction Scheme (19)



5

Example 3-3:

In the same manner as Example 2-3, conductive polymer layer PEDT/PPS was formed on a washed ITO-coated glass substrate. Thereon spin coated was a dichloroethane solution (1 mass%) having mixed therein 70 mass% of the phosphrescent polysilane obtained in Example 3-2 and 30 mass% of oxadiazole derivative OXD-7 (product name, manufactured by Nihon SiberHegner K.K.) represented by formula (8) below. After sufficient drying, electrode Ca(10nm)/Al(150nm) was formed. Thus obtained device was sealed and properties were measured. Blue light emitted from a phosphorescent unit was observed, and the value of the external quantum efficiency was 5%.



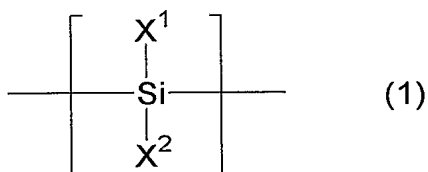
INDUSTRIAL APPLICABILITY

5 The phosphorescent polymer compound of the present invention, with chemical structural units having phosphorescent property being introduced in the polymer chains of silicone-base polymer, is stable and exhibits ultra-high efficiency in phosphorescence emission, especially blue phosphorescence
10 emission.

 Moreover, the organic EL device of the present invention, which is fabricated by wet-coating method using solution, realizes large-area display panel, high luminous efficiency and longer operating life, and therefore preferably applicable to
15 information display panel having a larger-area, lighting apparatus and the like.

CLAIMS

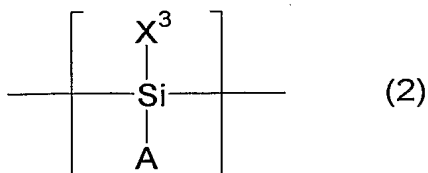
1. A phosphorescent polymer compound comprising a phosphorescent unit having phosphorescent property and a repeating unit represented by formula (1):



wherein X^1 and X^2 independently represent a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an amino group, a cyano group, a carboxyl group, a carbonyl group, a hydroxyl group, an aryl group which may be substituted, an aryloxy group which may be substituted or a heteroaryl group which may be substituted.

2. The phosphorescent polymer compound as claimed in claim 1, wherein the number of the phosphorescent unit (m) and the number of the repeating unit represented by formula (1) (n) have the following relationship : $0.0001 \leq m/(m+n) \leq 0.5$.

3. The phosphorescent polymer compound as claimed in claim 1 or 2, wherein the phosphorescent unit is a unit having an organic phosphorescent group in the side chain and represented by formula (2) below:



- wherein X^3 represents a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an amino group, a cyano group, a carboxyl

group, a carbonyl group, a hydroxyl group, an aryl group which may be substituted, an aryloxy group which may be substituted or a heteroaryl group which may be substituted, and A represents an organic phosphorescent group.

5

4. The phosphorescent polymer compound as claimed in any one of claims 1 to 3, wherein the phosphorescent unit has a complex structure of transition metal or rare-earth metal.

10

5. The phosphorescent polymer compound as claimed in any one of claims 1 to 4, which is soluble in organic solvent or water.

6. The phosphorescent polymer compound as claimed in any one of claims 1 to 5, having a polymerization degree of 5 to 5000.

15

7. A light-emitting material comprising the phosphorescent polymer compound as claimed in any one of claims 1 to 6.

20

8. The light-emitting material as claimed in claim 7, which further contains an organic compound having electron transporting property.

25

9. An organic electroluminescent (EL) device comprising one or more organic polymer layers between an anode and a cathode, wherein at least one of the organic polymer layers comprises the light-emitting material as claimed in claim 7 or 8.

30

10. The organic EL device as claimed in claim 9, wherein the anode is formed on a plastic substrate.

11. The organic EL device as claimed in claim 9 or 10, wherein the organic polymer layer(s) is(are) formed by a coating method.

12. An active-matrix display apparatus comprising the organic EL device as claimed in any one of claims 9 to 11 and a thin film transistor.

5

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 03/05352

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H05B33/14 C09K11/06 H01L51/20 H01L51/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H05B C09K H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DJUROVICH P I ET AL: "IR(III) CYCLOMETALATED COMPLEXES AS EFFICIENT PHOSPHORESCENT EMITTERS IN POLYMER BLEND AND ORGANIC LEDS" POLYMER PREPRINTS, AMERICAN CHEMICAL SOCIETY, US, vol. 41, no. 1, March 2000 (2000-03), pages 770-771, XP001052648 ISSN: 0032-3934 cited in the application * page 770, Experimental, Figure 1 *	1-12
Y	WO 02 02714 A (PETROV VIACHESLAV A ;DU PONT (US); WANG YING (US); GRUSHIN VLADIMI) 10 January 2002 (2002-01-10) * page 12, lines 12-30 *	1-12

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

31 July 2003

Date of mailing of the international search report

21/08/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Nemes, C

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 03/05352

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2002/024293 A1 (MIYASHITA YOUSUKE ET AL) 28 February 2002 (2002-02-28) * the entire document * ---	1-12
A	WO 01 41512 A (UNIV PRINCETON ;UNIV SOUTHERN CALIFORNIA (US)) 7 June 2001 (2001-06-07) * the entire document * ---	1-12
A	US 2001/019782 A1 (KIMURA KEIZO ET AL) 6 September 2001 (2001-09-06) * the entire document * -----	1-12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP 03/05352

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Present claims 1-12 relate to an extremely large number of possible compounds/products/devices. In fact, the claims contain so many options, variables, and possible permutations that a lack of clarity within the meaning of Article 6 PCT arises to such an extent as to render a meaningful search of the claims impossible. Because of the lack of explicit structural features in the definition of the phosphorescent unit, it is impossible to formulate an adequate structural drawing of said unit that would be suitable for a meaningful search. Consequently, the search has been carried out only for the compounds explicitly disclosed in the application (Examples 1-2, 1-3, 2-2, 2-3, 3-2, and 3-3).

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 03/05352

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